

# DETERMINATION OF STRUCTURAL DEFECTS IN PHYLLOSILICATES BY X-RAY POWDER DIFFRACTION—I. PRINCIPLE OF CALCULATION OF THE DIFFRACTION PHENOMENON

A. PLANÇON and C. TCHOUBAR

Laboratoire de Cristallographie, Université d'Orléans et Centre de Recherche sur les Solides à  
Organisation Cristalline Imparfaite, C.N.R.S. 45045 Orléans Cedex, France

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**Abstract**—This paper describes the calculation of the diffracted intensity for models of powdered minerals with lamellar structure, in order to compare experimental and theoretical X-ray diagrams. The calculation takes into account at the same time (i) the possibility of coexistence of different kinds of layers in the stackings, (ii) the possibility of stacking faults between the layers (translative or rotative ones) and (iii) the unavoidable orientation of particles in the powder sample (the method of determination of the orientation is described).

## INTRODUCTION

It is known that, to explain several peculiar physical or physico-chemical properties of phyllosilicates, it is necessary to resolve not only the **mean** crystalline structure of these minerals, but their **real** structure, that is to say the nature and distribution of the structural defects. Numerous authors have developed the theory of X-ray powder diffraction by partially ordered layer structures. For the determination of the 'disorder parameters', two chief methods are used. They are based on the analysis of the intensity distribution considered as a **continuous** function in reciprocal space.

(1) The first method consists in the description of the organization of the solid by direct determination of  $P(\mathbf{r})$ , the probability distribution of interatomic distances in the studied substance.  $P(\mathbf{r})$  is the generalized form of the Patterson distribution and is obtained by Fourier transform of the  $i(\mathbf{s})$  intensity distribution. This method, introduced by Zernicke and Prins (1927) is particularly suited for the determination of the atomic organization in a small range of distances. Nevertheless, it is readily applicable only in the case of simple structures. Moreover, in this method it is critical to take account of the different disturbing functions related to the experimental installation (sample shape, instrumental aberrations introduced by the optical system, etc.). Finally, in the case of layer silicates which have a pseudo-hexagonal distribution of reflection symmetry, the direct exploitation of the diffracted intensity is almost impossible when they are microcrystallized, allowing only powder patterns to be obtained.

(2) The second method is an indirect one which consists in choosing theoretical models for the atomic organization and calculating the intensities corresponding to such models. Then, after introduction of perturbation functions, the theoretical distribution of

intensities is compared with the experimental one. This method permits one to interpret rather easily the observed diffraction, mainly when order remains in the structure, in one or two dimensions, as in phyllosilicates. Moreover, this method is also applicable to powdered minerals.

In this first part, we intend to show the principle of calculation of the intensity diffracted by models of a powdered mineral with lamellar structure, by using the results of several authors and our own recent ones. We shall envision several kinds of structural defects, and show the effects of a partial orientation of particles in the powder and of the coexistence of layers of different nature inside each stacking.

## GENERAL FEATURES OF THE DIFFRACTION

The diffraction phenomenon produced by a stacking of  $M$  parallel layers is described by the interference of the waves diffracted by each one of the layers in the stacking (Hendricks and Teller, 1942; Mering, 1949). The amplitude diffracted by one single layer (where the vectors defining the cell are  $\mathbf{a}$  and  $\mathbf{b}$ ) takes non-negligible values only in cylindrical domains, normal to the  $\pi$  plane of the reciprocal lattice ( $\mathbf{a}^*$ ,  $\mathbf{b}^*$ ), and passing by the nodes  $hk$  of this lattice (Figure 1). Along a cylindrical ( $hk$ ) domain, this amplitude is:

$$\phi_{hk}(Z) = \frac{1}{\Omega} F_{hk}(Z) D(\mathbf{u}), \quad (1)$$

where  $F_{hk}(Z)$  is the Fourier transform of the base unit of the structure (or structure factor) at the height  $Z$  over the reciprocal plane  $\pi$ ,  $\Omega = |\mathbf{a} \wedge \mathbf{b}|$  is the surface of the cell of the layer.  $D(\mathbf{u})$  is the shape transform (Fourier transform of the shape function of the layer),  $\mathbf{u}$  is the vector which fixes, in the  $\pi$  plane, a point

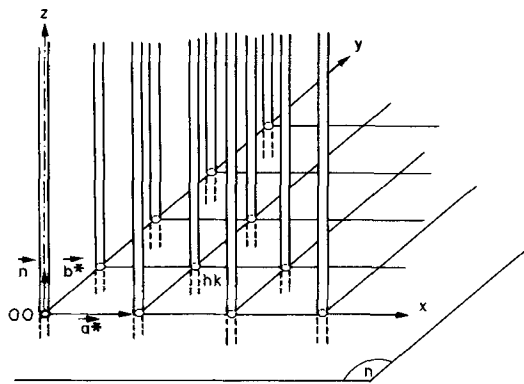


Figure 1. Amplitude cylinders of a biperiodic layer.

of the  $(hk)$  cylinder; the origin of  $\mathbf{u}$  is taken at the  $hk$  geometrical node.

If we define  $\phi(\mathbf{s})$  as the set of cylindrical domains in which the intensity diffracted by a layer is not negligible, then the intensity diffracted by a stacking of  $M$  layers is given by:

$$i(\mathbf{s}) = \sum_{m=1}^M \sum_{m'=1}^M \phi_m(\mathbf{s}) \phi_{m'}^*(\mathbf{s}) \exp[-2\pi i \mathbf{s} \cdot (\mathbf{r}_m - \mathbf{r}_{m'})].$$

$\phi_m(\mathbf{s})$  is the Fourier transform of the  $m$ th layer in the stacking,  $\mathbf{r}_m$  is the vector which fixes the position of the  $m$ th layer relative to an arbitrary origin 0 (see Figure 2),  $\mathbf{s}$  is the diffusion vector of modulus  $2 \sin \theta / \lambda$ .

For a great number of stackings with the same thickness, not interfering between them (case of a powder), the mean intensity diffracted by a stacking is:

$$\bar{i}(\mathbf{s}) = \sum_{m=1}^M \sum_{m'=1}^M \overline{\phi_m(\mathbf{s}) \phi_{m'}^*(\mathbf{s}) \exp[-2\pi i \mathbf{s} \cdot (\mathbf{r}_m - \mathbf{r}_{m'})]} \quad (2)$$

or

$$\bar{i}(\mathbf{s}) = \sum_{m=1}^M \sum_{m'=1}^M \overline{F_m(\mathbf{s}) F_{m'}^*(\mathbf{s}) D_m(\mathbf{u}) D_{m'}^*(\mathbf{u}) \exp[-2\pi i \mathbf{s} \cdot (\mathbf{r}_m - \mathbf{r}_{m'})]} \quad (3)$$

In the general case, the stackings are constituted by different kinds of layers. Then, the structure factors  $F_m(\mathbf{s})$  are different.

The expression (3) shows that the diffraction phenomenon produced by a stacking can be related in a relatively simple way to: the nature of layers [by the structure factors  $F_m(\mathbf{s})$ ], the dimensions of layers [by the shape transform  $D_m(\mathbf{u})$ ], and finally to the stacking mode (by the exponential term which expresses the interference of waves diffracted by layers, and which varies with their relative positions).

Thus, the determination of the nature and proportion of stacking defects in a microcrystallized lamellar mineral consists of three steps: (i) the calculation of

the intensity  $\bar{i}(\mathbf{s})$  which should be diffracted by a model of stacking of layers, (ii) the derivation, from  $\bar{i}(\mathbf{s})$ , of the intensity  $I(\mathbf{s})$  diffracted by a powder, and (iii) the comparison of this theoretical intensity with the experimental one.

PRINCIPLE OF CALCULATION OF THE AVERAGE INTENSITY DIFFRACTED BY A STACKING

Case of a stacking constituted by identical layers

The simplest hypothesis consists of assuming that the phyllosilicate sample is constituted by stackings having an average of  $M$  identical layers only shifted relative to each other. In this case, the structure factors  $F_m$  are identical for all the layers, and the expression (2) of the average intensity diffracted by a stacking is simplified to:

$$\bar{i}(\mathbf{s}) = \phi(\mathbf{s}) \phi^*(\mathbf{s}) \sum_{m=1}^M \sum_{m'=1}^M \overline{\exp[-2\pi i \mathbf{s} \cdot (\mathbf{r}_m - \mathbf{r}_{m'})]} = M \phi(\mathbf{s}) \phi^*(\mathbf{s}) G(\mathbf{s}). \quad (4)$$

$G(\mathbf{s})$ , named 'modulation function', expresses the interference phenomenon between the layers of the stacking and takes into account their eventual translative faults. The expression of the  $G(\mathbf{s})$  function has been established by Mering (1949) and subsequently by the authors (Plançon and Tchoubar, 1975), in the case where there does not exist any correlation between the translations of successive layers (interaction only between first neighbouring layers). So, the expression (4) allows the calculation of the intensity diffracted by models containing only translative stacking faults without correlation between them.

Case of a stacking constituted by layers of different nature

For stackings constituted either by layers of different nature or by identical layers rotated in their plane, the development of the expression (2) which allows the calculation of the diffracted intensity demands the use of matrices (Hendricks and Teller, 1942; Kakinoki

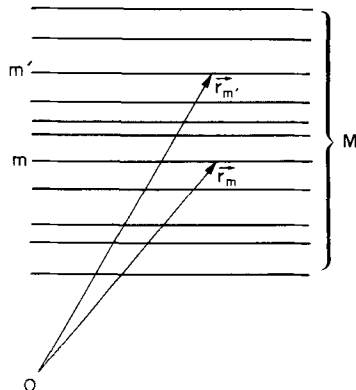


Figure 2. Schematic representation of a stacking containing  $M$  layers.

and Komura, 1952; Plançon and Tchoubar, 1976). In the hypothesis of a no-correlation between the defects, the intensity diffracted by a stacking of  $M$  layers can be written:

$$\bar{i}(\mathbf{s}) = M \operatorname{spur} \operatorname{Re}\{\Phi PR\}, \tag{5}$$

where  $\Phi, P, R$  are square matrices of  $g$  order equal to the  $g$  types of different layers in the stacking, and where  $\operatorname{Re}$  corresponds to the real part of the product  $\Phi PR$ .

In the  $\Phi$  matrix, the  $m_{ij}$  term ( $i$  row,  $j$  column) is equal to the product  $\phi_i^*(\mathbf{s}) \phi_j(\mathbf{s})$  of the amplitude diffused by a layer of  $j$  type by the conjugated amplitude diffused by a layer of  $i$  type (obviously  $1 \leq i \leq g$  and  $1 \leq j \leq g$ ).

$P$  is a diagonal matrix, whose  $m_{ii}$  element is equal to the proportion of  $i$  layers in the stacking.

$R$  is a matrix equal to (Plançon and Tchoubar, 1976)

$$R = I + 2Q(I - Q)^{-1} + \frac{2}{M}(Q^{M+1} - Q)(I - Q)^{-2}.$$

In this expression,  $I$  is the unit matrix and  $Q$  is a matrix which expresses the interferential phenomenon between first neighbouring layers. Its  $m_{ij}$  term is equal to

$$\sum_k p_{ij}^k \exp[2\pi i \mathbf{s} \cdot \mathbf{t}_{ij}^k],$$

where  $\sum_k$  is a summation done over the whole set of possible translations between an  $i$  layer and a  $j$  first neighbouring layer.

$\mathbf{t}_{ij}^k$  is one of these translations and  $p_{ij}^k$  its probability.

If we call  $\alpha_{ij}(\mathbf{s})$  the  $m_{ij}$  term of the  $PR$  matrix, the expression (5) of the diffracted intensity becomes:

$$i(\mathbf{s}) = M \operatorname{Re} \sum_{i=1}^g \sum_{j=1}^g \phi_i(\mathbf{s}) \phi_j^*(\mathbf{s}) \alpha_{ij}(\mathbf{s})$$

or

$$i(\mathbf{s}) = M \operatorname{Re} \sum_{i=1}^g \sum_{j=1}^g F_i(\mathbf{s}) F_j^*(\mathbf{s}) D_i(\mathbf{u}) D_j^*(\mathbf{u}) \alpha_{ij}(\mathbf{s}), \tag{6}$$

where  $F_i(\mathbf{s})$  and  $F_j(\mathbf{s})$  are respectively the structure factors of layers of  $i$  and  $j$  types.

$\alpha_{ij}(\mathbf{s})$  which expresses the interferential phenomenon between all the layers of  $i$  and  $j$  types inside a stacking is the analogous for these layers to the  $G(\mathbf{s})$  modulation function introduced in the expression (4).

The relation (6) allows the calculation of the intensity diffracted by any stacking model containing simultaneously layers of different nature and translative or rotative stacking faults (Plançon and Tchoubar, 1976).

**PRINCIPLE OF CALCULATION OF THE INTENSITY DIFFRACTED BY A POWDER**

*Numerical integration of Brindley and Mering (1951)*

In order to deduce the intensity diffracted by a powder from the intensity diffracted by a stacking,

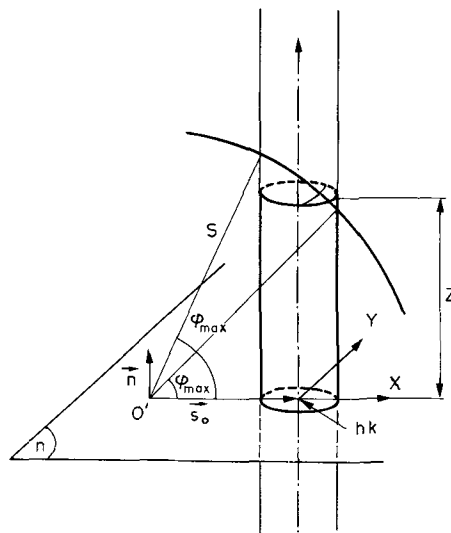


Figure 3. Schematic representation of a  $(hk)$  cylinder cut by an integration sphere with radius  $s = 2 \sin \theta/\lambda$ .

it is necessary to consider the intersection of the Ewald sphere by the cylindrical domains  $(hk)$ , when these turn around the origin of the reciprocal space. In fact, several authors (Laue, 1932; Warren, 1941; Wilson, 1949a,b; Brindley and Mering, 1951) have shown that it amounts to the same thing to keep fixed cylinders  $(hk)$  and to consider their intersection with spheres of center  $O'$  and increasing radius  $s$  (Figure 3).

In the simplest case of stackings constituted by identical layers, the powder intensity diffracted at the  $2\theta$  angle by a  $(hk)$  cylinder is proportional to:

$$I_{hk}(s) \simeq \int i_{hk}(s, \varphi) \frac{dA}{4\pi s^2},$$

where  $dA$  is an element of the surface common to the sphere of radius  $s$  and to the  $(hk)$  cylinder, and  $\varphi$  is the angle between  $\mathbf{s}$  and the  $\pi$  plane, for a fixed  $Z$  height.

By using relations (4) and (1), this  $I_{hk}(s)$  intensity becomes:

$$I_{hk}(s) = \int MF_{hk}(Z) F_{hk}^*(Z) D(\mathbf{u}) D^*(\mathbf{u}) G_{hk}(Z) \frac{dA}{4\pi s^2}. \tag{7}$$

By replacement of vector  $\mathbf{u}$  by its components  $X$  and  $Y$ , respectively parallel and normal to the vector  $(\mathbf{s}_0)_{hk}$ , which joins the origin  $O'$  of the reciprocal space to the  $hk$  geometrical node, Brindley and Mering (1951) show that the expression (7) can be written

$$I_{hk}(s) = \frac{M}{4\pi s} \int |F_{hk}(Z)|^2 G_{hk}(Z) T(X) d\varphi. \tag{8}$$

The integration is done between the two  $\varphi_{\min}$  and  $\varphi_{\max}$  angles which correspond to the boundaries of the intersection of the radius  $\mathbf{s}$  with the  $(hk)$  cylinder (Figure 3).

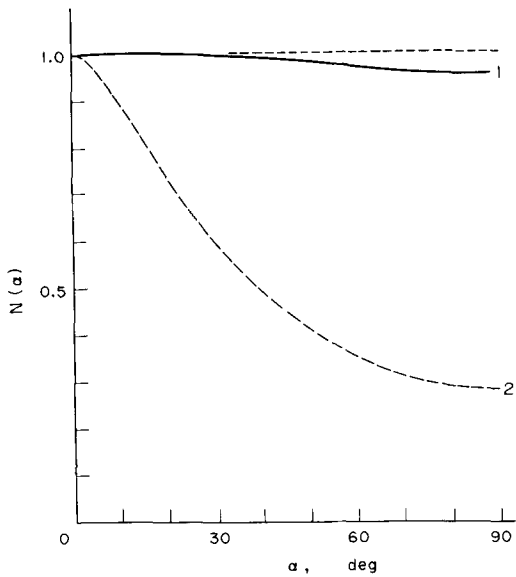


Figure 4. Orientation curves of particles in a powder for a well-crystallized kaolinite; curve 1, sample prepared by freeze-drying of an aqueous suspension; curve 2, sample prepared from the same kaolinite, but not freeze-dried; dotted line: theoretical value corresponding to a completely disoriented sample.

$T(X) = \int D(X, Y) D^*(X, Y) dY$  is, by definition, the projection of the transversal section of the  $(hk)$  cylindrical domain on the direction of the  $(s_0)_{hk}$  vector. This  $T(X)$  function expresses the influence of the shape and of the size of the diffraction layer on the intensity distribution.

Yet, the expression (8) does not take into account two difficulties frequently met, in the study of micro-crystallized silicates. First of all, those minerals have frequently a strong anisotropic shape such as thin plaquettes: consequently, a partial orientation of particles in the powder is practically inevitable. On the other hand, the amplitude cylinders corresponding to different layers of the same stacking and which interfere between themselves can be in only partial coincidence. This arises because either the layers are not of the same nature and have slightly different parameters, or there exist, inside the stacking, some rotations of layers such as to cause the amplitude cylinders to be not in a strict superposition (this can happen, particularly, in smectites).

#### Effect of a partial orientation of particles in the powder

Different authors (Brindley and Kurtossy, 1961; Taylor and Norrish, 1966; Lippmann, 1970) have proposed methods of measurement of the orientation in a powder. A simple method (de Courville *et al.*, to be published) consists in the determination of the  $(I_{001})_s$  area of the 001 reflection when the plane of the sample is put in the X-ray beam in a position

of **symmetrical transmission**; then, this area is compared to the  $(I_{001})_{ns}$  area measured for the same reflection when the plane of the sample occupies diverse positions of **non symmetrical transmission**. After correction for the absorption and for the modification of diffracting volume, it is possible to infer from the ratio  $(I_{001})_{ns}/(I_{001})_s$  a  $N(\alpha)$  function which is a measure of the orientation of the particles in the powder ( $\alpha$  is the angle of the basal  $\pi$  plane of a particle with the plane of the sample). For illustration, we give in Figure 4 the  $N(\alpha)$  curves determined experimentally for two samples of the same well-crystallized kaolinite. The curve 1 corresponds to a powder obtained by freeze-drying of a suspension of the mineral in water: one observes an almost complete disorientation of the particles [the complete disorientation corresponds to  $N(\alpha) = 1$  (horizontal dotted line) for all  $\alpha$  angles]; the curve 2 corresponds to a sample prepared directly from a powder of the same kaolinite that was not subjected to freeze-drying.

The existence of a partial orientation of plaquettes in the powder leads to a modification of the expression (8) given by Brindley and Mering, under the form:\*

$$I_{hk}(s) \simeq \frac{M}{4\pi s} \int N(\varphi) |F_{hk}(Z)|^2 G_{hk}(Z) T(X) d\varphi. \quad (9)$$

The  $N(\varphi)$  function, introduced in the expression (9) expresses the fact that there exists, in the powder, an 'infinity' of particles for which the  $(hk)$  cylinder is cut at the same  $Z$  height by the Ewald sphere (Figure 5). These are all the particles whose  $\pi$  plane makes the angle  $\varphi$  with the diffusion vector  $s$  (these  $\pi$  planes are tangent to the cone of  $s$  axis and top half angle  $\varphi$ ) each one making, with the plane of the sample, an angle  $\alpha$  included between  $\varphi$  and  $\pi - \varphi$ .

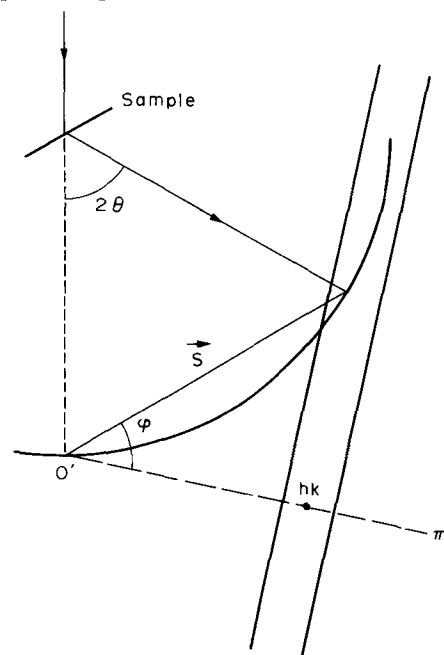


Figure 5. Intersection of Ewald sphere by an  $(hk)$  cylinder.

\* The details of the method are described in the Ph.D. thesis of Plançon (1976, Université d'Orléans, France) and will be published later.

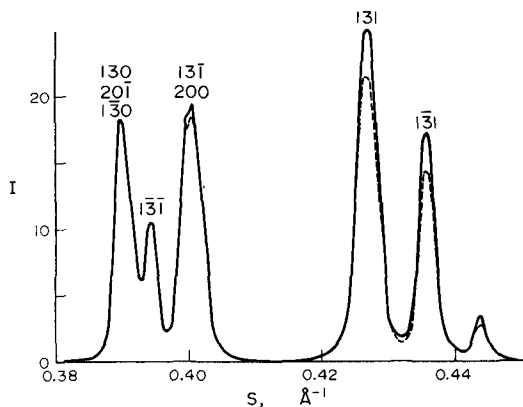


Figure 6. Effect of the orientation on the  $20(l)$ ,  $13(l)$  calculated profiles of a well-crystallized kaolinite.

For a sample studied by transmission, the  $N(\varphi)$  function is inferred from the  $N(\alpha)$  function by:

$$N(\varphi) = \int_{\psi=0}^{\psi=2\pi} N(\alpha) d\psi,$$

where, for a value of  $\varphi$ , the angle  $\alpha$  is calculated for each  $\psi$  value by the relation

$$\cos \alpha = \cos \varphi \cos \psi.$$

Figure 6 illustrates the influence of a partial orientation of particles on the powder reflections' profile. In this figure, we have shown by a full line the calculated profile of the  $20(l)$ ,  $13(l)$  reflections of a well-crystallized kaolinite† in the case of almost complete disorientation characterized by curve 1 of Figure 4. The dotted line corresponds to the calculated profile in the case of a particles' orientation characterized by the curve 2 of the same figure.

#### Case of stackings constituted by layers of different nature showing eventually a partial superposition of amplitude cylinders

We have pointed out above that, when a stacking is constituted of layers of different natures, the average intensity diffracted by a stacking is given by the expression (6). In this case, the  $I_{hk}(s)$  intensity diffracted under a  $2\theta$  angle by the powder, takes the form

$$I_{hk}(s) \simeq \frac{M}{4\pi s} \operatorname{Re} \sum_{i=1}^g \sum_{j=1}^g \int [F_{hk}(Z)]_i \times [F_{hk}^*(Z)]_j \alpha_{ij}(Z) T_{ij}(X) d\varphi \quad (10)$$

with

$$T_{ij}(X) = \int D_i(X, Y) D_j^*(X, Y) dY.$$

$T_{ij}(X)$  is equivalent to the  $T(X)$  function of Brindley and Mering when all the amplitude cylinders of the different layers of  $i$  and  $j$  nature are in a rigorous

superposition. On the contrary, the  $T_{ij}(X)$  function needs to be calculated separately for each pair of  $h$  and  $k$  indexes when there exists only a partial coincidence of the amplitude cylinders (Plançon *et al.*, to be published).

#### CONCLUSION

The principle of calculation presented in this paper, based on the hypothesis of an absence of correlation between defects, allows the determination of the intensity diffracted by a powder, taking into account at the same time the different natures of the layers, the stacking faults (translative or rotative ones) and the partial orientation of the particles in the powder.

Nevertheless, we draw attention to two points:

(1) in order to compare a calculated profile with an experimental one, it is necessary that this last one should not be deformed by the recording. It is then necessary to determine the best experimental conditions (choice of the thickness of the sample, etc.) and to use an installation adapted to such a study (diffractometer with monochromator and stepwise counter, adjustment of the slits, etc.).

(2) This method, based on the research of the stacking model which leads to a good fit between the experimental and theoretical profiles, is really efficient only when the diffraction pattern is not studied in a narrow domain. For example, in the case of kaolinites whose diagrams show some different characteristics for the  $hk(l)$  reflections with  $k$  multiple of 3 or not a multiple of 3, the method of models can be used only if the study includes, beyond the  $02(l)$ ,  $11(l)$  reflections, also the  $20(l)$ ,  $13(l)$  reflections (that is to say that the study must include two sets of zones with different characteristics).

Part II of this work will be an application of part I, devoted to the qualitative and quantitative study of structural defects in natural kaolinites more or less disordered.

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† The accurate description of this kaolinite will be put in part II of this paper.

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