Stacking Faults in $Ca(OH)_2$ Produced by Vapour Phase Hydration

G. Spinolo and U. Anselmi Tamburini

Dipartimento di Chimica Fisica dell' Universita' and Centro di Studi per la Termodinamica ed Elettrochimica dei Sistemi Salini Fusi e Solidi del C.N.R., Pavia, Italy

Z. Naturforsch. **40 a**, 73–78 (1985); received October 25, 1984

The diffraction profiles of a thin single crystal with stacking faults were calculated with the theory of diffraction of a one-dimensionally disordered crystal (Kakinoki, Komura, Allegra) by including the effect of crystallite thickness. The results hold for generalized close packed structures.

An application to calcium hydroxide is discussed: the stacking faults significantly contribute to the disorder of poorly crystalline forms of $Ca(OH)_2$ produced by reaction of calcium oxide with water vapour at room temperature.

1. Introduction

Endothermic decompositions of the type

$$A\,(solid) \rightarrow B\,(solid) + C\,(gas)$$

and their reverse reactions

$$B\,(solid) + C\,(gas) \rightarrow A\,(solid)$$

often produce [1] solid materials characterized by large chemical reactivity, and by various crystal imperfections such as small crystallite sizes and microstrains. In this case, both kinds of imperfections can be simultaneously determined with the broadening analysis of X-ray powder diffractograms, e.g., from the knowledge of the Fourier transforms of some (suitably chosen) diffraction lines [2].

In a previous investigation [3] on calcium hydroxide produced by CaO vapour phase hydration, evidence was obtained for the fact that the above mentioned kinds of defects cannot fully explain the experimental diffraction profiles. On a purely analogical basis, we indicated that a third kind of crystalline imperfection (disorder of the stacking sequence) is probably involved.

Generally speaking, the diffraction profiles of structures built up with an arbitrary stacking sequence of simple or complex layers can be calculated with the theory of diffraction of a one-dimensionally disordered crystal. This is a well established topic [4], which received contributions from several Authors (see, e.g., [5–9]); applications deal with polytypism in disordered crystals, with antiphase boundaries in ordered solutions, and with complex stacking faults in hexagonal or cubic structures.

However, the final results of the theory are generally worked out for large crystals, and are not directly suitable – in their present form – for the investigation of a sample of small-sized crystallites.

In the present work, we shall show first how this limit can be removed for a large class of materials (provided that their structures are close packed in the generalized sense defined in the following section); moreover, we shall apply this result to our previous investigation in order to prove that the $Ca(OH)_2$ particles obtained from CaO with a (highly irreversible) gas–solid reaction exhibit both small crystallite sizes and a detectable amount of stacking disorder.

2. Diffraction from a Thin Single Crystal with Layer Disorder

It is worth recalling here some significant points of the theory of diffraction from monodimensionally disordered crystals as presented by Allegra [7], and Kakinoki and Komura [8, 9].

This theory looks at each particular structure as built up with a set of parallel layers having the same two-dimensional cell. Two layers may differ from

Reprint requests to Prof. Giorgio Spinolo, Dipartimento di Chimica Fisica dell' Universita', Viale Taramelli, 16, I-27100 Pavia/Italien.

0340-4811 / 85 / 0100-0073 $ 01.30/0. – Please order a reprint rather than making your own copy.

each other either because they contain different arrangements of atoms or ions, or because they have the same content although being reciprocally misplaced.

In the "equal thickness" case (which differs from the most general case inasmuch as the layers are assumed to have all the same thickness along c, i.e., the crystallographic axis perpendicular to the layers), the intensity equation becomes

$$I(\varphi) = \sum_{m=0}^{N-1} (N-m) \exp(-i\, m\, \varphi)\, J_m + \text{conj.} \qquad (1)$$

$$J_m = \text{tr}\,(\boldsymbol{V}\boldsymbol{F}\boldsymbol{P}^m)\,,$$

where

$\boldsymbol{F}_{ii}$ is the existence probability of a (type i) layer,
h, k, l are the Miller indexes,
N is the number of layers in the crystals,
$\boldsymbol{P}_{ij}$ is the continuing probability of layer j after layer i,
$\boldsymbol{V}_{ij} = V(i)\, V^*(j)$,
$V(i)$ is the form factor of layer i, and
$\varphi = 2\pi l$.

In the "displacement stacking faults" case it is furthermore assumed that the bidimensional cells of the layers are hexagonal and differ only because their origins are displaced by vectors $\boldsymbol{u}_i$:

$$\boldsymbol{u}_i = i\,(\boldsymbol{a}/3 + 2\boldsymbol{b}/3)\,; \quad (i = 1, 2)\,. \qquad (2)$$

In other words, their origins must be placed at the positions denoted by letters A, B and C in the usual notation of close packed structures.

As a matter of fact, most of the practically interesting problems belong to a somewhat intermediate case, denoted in the following as "generalized close packed structures"*. Here, a monodimensionally disordered crystal is built up with a few "simple" hexagonal layers which are joined together (e.g., by stoichiometry) to form a restricted number of "complex" layers, obey to the "equal thickness" requirement, and contain the same types of "simple" layers in the same order.

The various complex layers (hereafter denoted as "kinds of layer") may differ from one another because, on going from a given complex layer to another, it may happen either

a) that all the constituent simple layers have been displaced by the same $\boldsymbol{u}_i$ vector (i.e., that the complex layer has been displaced as a whole)**, or
b) that different displacements have occurred for each constituent simple layer.

Allegra [7] has shown how to profit from the regularities of generalized close packed structures to get a more manageable form of (1).

The present work gives a more direct treatment of the problem, based on the inspection of the symmetry that the $\boldsymbol{V}$, $\boldsymbol{F}$ and $\boldsymbol{P}$ matrices take up as a consequence of the properties of generalized close packed structures. Because of the different treatment, the usual requirement to take the limit $N \to \infty$ (N = number of complex layers in the actual crystal) is not employed and (1) can be worked out for an arbitrary (finite or infinite) value of N, thus giving the desired application of the theory to the diffraction from thin crystallites.

It is worth specifying here that we do not leave the basic assumption of a monodimensional disorder: both kinds of crystal imperfections (i.e., small particle sizes and faults) are only relevant to the c axis. In other words, we explicitly assume both that the stacking faults extend over the whole crystal and that the crystal thickness is finite only along the crystallographic direction perpendicular to the layers.

Let us now consider the particular structure of the $\boldsymbol{V}$, $\boldsymbol{F}$, and $\boldsymbol{P}$ matrices: when they are partitioned into nine smaller $(n \times n)$ matrices, it turns out that only three of them are distinct, because the row of the partition contain the same submatrices in different cyclic permutations, as indicated in the following equation:

$$\boldsymbol{X} = \begin{pmatrix} {}^1\boldsymbol{x} & {}^2\boldsymbol{x} & {}^3\boldsymbol{x} \\ {}^3\boldsymbol{x} & {}^1\boldsymbol{x} & {}^2\boldsymbol{x} \\ {}^2\boldsymbol{x} & {}^3\boldsymbol{x} & {}^1\boldsymbol{x} \end{pmatrix}. \qquad (3)$$

* This name does not imply that these structures have anything to do with the densest packings of hard spheres, although the usual close packed structures are a particular case of this problem.

** This procedure can be applied twice to a given complex layer, so that the set of all possible "kinds of layer" can be partitioned either into three groups of n elements, or into n groups of three elements. Hereafter we will assume that the $(R = 3n)$ kinds of layer are suitably ordered [9] by considering a partition into three groups of n elements, so that the kinds placed at positions $j + n$ and $j + 2n$ $(j = 1, \ldots, n)$ are respectively obtained by applying the $\boldsymbol{u}_1$ or the $\boldsymbol{u}_2$ displacements to the kind placed at position j.

For the sake of brevity, this feature will be written as

$$\boldsymbol{X} = G\,({}^1\boldsymbol{x}, {}^2\boldsymbol{x}, {}^3\boldsymbol{x})\,. \tag{4}$$

In particular:

$$\boldsymbol{F} = G\,(\boldsymbol{f}, \boldsymbol{0}, \boldsymbol{0})\,; \quad \boldsymbol{f} = R^{-1}\,\boldsymbol{I}_n\,. \tag{5}$$

($\boldsymbol{I}_n$ being the n-order unit matrix.)

$$\boldsymbol{V} = G\,(\boldsymbol{v}, \varepsilon\,\boldsymbol{v}, \varepsilon^*\,\boldsymbol{v})\,; \tag{6}$$

and

$$\boldsymbol{P} = G\,({}^1\boldsymbol{p}, {}^2\boldsymbol{p}, {}^3\boldsymbol{p})\,. \tag{7}$$

Let us define

$$\boldsymbol{h} \equiv \boldsymbol{v}\,\boldsymbol{f}, \tag{8}$$

$$\boldsymbol{p} \equiv {}^1\boldsymbol{p} + \varepsilon^*\,{}^2\boldsymbol{p} + \varepsilon\,{}^3\boldsymbol{p}\,, \tag{9}$$

and

$$\boldsymbol{T}_m \equiv \boldsymbol{V}\,\boldsymbol{F}\,\boldsymbol{P}^m. \tag{10}$$

Matrices defined by (3) have some interesting properties that can be easily verified and that greatly help in simplifying (1). Indeed, the product of two such matrices is again a matrix with this structure:

$$G\,({}^1\boldsymbol{x}, {}^2\boldsymbol{x}, {}^3\boldsymbol{x})\;G\,({}^1\boldsymbol{y}, {}^2\boldsymbol{y}, {}^3\boldsymbol{y}) = G\,({}^1\boldsymbol{z}, {}^2\boldsymbol{z}, {}^3\boldsymbol{z})\,. \tag{11}$$

In particular

$$\boldsymbol{T}_m = G\,({}^1\boldsymbol{t}_m, {}^2\boldsymbol{t}_m, {}^3\boldsymbol{t}_m)\,. \tag{12}$$

Moreover, by mathematical induction:

$${}^1\boldsymbol{t}_m = \boldsymbol{h}\,\boldsymbol{p}^m; \quad {}^2\boldsymbol{t}_m = \varepsilon\,{}^1\boldsymbol{t}_m\,; \quad {}^3\boldsymbol{t}_m = \varepsilon^*\,{}^1\boldsymbol{t}_m \tag{13}$$

and

$$J_m = \mathrm{tr}\,(\boldsymbol{V}\,\boldsymbol{F}\,\boldsymbol{P}^m) = 3\;\mathrm{tr}\,(\boldsymbol{h}\,\boldsymbol{p}^m)\,. \tag{14}$$

Equation (14) represents a remarkable improvement over (1) because it is an n-dimensional, instead of an R-dimensional ($R = 3n$) problem. Moreover, if a (non singular) o matrix exists such that

$$\boldsymbol{o}\,\boldsymbol{p}\,\boldsymbol{o}^{-1} = \boldsymbol{q} = \mathrm{diag}\,(q_1, \ldots, q_n) \tag{15}$$

we have

$$\mathrm{tr}\,(\boldsymbol{h}\,\boldsymbol{p}^m) = \sum_{j=1}^{n} r_{jj}\,(q_j)^m\,, \tag{16}$$

where

$$\boldsymbol{r} \equiv \boldsymbol{o}\,\boldsymbol{h}\,\boldsymbol{o}^{-1}\,. \tag{17}$$

Equation (1) is then reduced to the sum of a geometric series, thus giving in a straightforward way

$$N^{-1}\,I\,(l) = \mathrm{Re}\left\{\sum_{j=1}^{n} \alpha_j\,(1-\beta_j)^{-1}\right. \tag{18}$$
$$\left.\cdot\,[1 + \beta_j\,N^{-1}\,(\beta_j^N - 1)\,(1-\beta_j)^{-1}]\right\}\,,$$

where

$$\alpha_j = 6\,R^{-1}\,r_{jj}\,; \quad \beta_j = q_j\,\exp\,(-\,i\,\Phi)\,. \tag{19}$$

Note that in (18) the intensity has been normalized and its dependence on the Miller index l made explicit (l is a continuous variable). Caution is necessary in evaluating the diffraction intensity with (18) when $\beta_j = 1$ or when $\det\,(\boldsymbol{o}) = 0$.

Equation (18) gives the required link between the theory of diffraction from monodimensionally disordered crystals and the powder method, as particle sizes (along c) and stacking faults are taken into account at the same time.

Starting from (18), X-ray powder diffraction profiles may be calculated

a) by applying the powder pattern power theorem [2], and
b) by summing up the intensities of the different $h\,k$ rows within the diffraction sphere.

3. Results and Discussion

We can now discuss (18) in connection with our problem of small-sized and faulted particles of $Ca(OH)_2$.

The regular structure of this compound corresponds to the indefinite repetition of the same "minimal sandwich" of two anionic layers and one intermediate cationic layer placed in three different (A, B, C) positions*.

A discussion of the stacking disorder needs some preliminary statements about the order of influence between the layers. Failing a specific information, we can start by taking into account the simplest case of influence between a given "minimal sandwich" and its nearest neighbours only. Accordingly, the possible configurations of the minimal sandwiches are also the fundamental "kinds" of complex layer. These kinds are six, and are represented by the sequences ($\mathrm{A}\,\gamma\,\mathrm{B}$), ($\mathrm{B}\,\gamma\,\mathrm{A}$), and by those obtainable with cyclic permutation of the letters (following a common practice, Roman letters stand for the

* $Ca(OH)_2$ has a crystal structure [10] usually named CdI_2-type although this is not the most common polytype of the latter compound [11]. Indeed, $Ca(OH)_2$ is isostructural with the smallest polytype (2H) of cadmium iodide. Figure 1 schematically shows the projections onto a (110) plane of the stacking sequences of this material and of some other polytypes frequently found in structurally related compounds such as CdI_2, $CdCl_2$ or PbI_2.

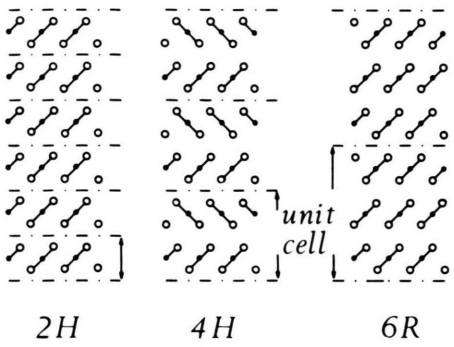

Fig. 1. Stacking sequence of some polytypes of MX_2 compounds. Empty circles: M^{++}; filled circles: X^-.

anionic layers, and Greek letters for the cationic ones). They will be indicated more concisely by the Greek letter of the intermediate cationic layer, primed or unprimed depending on whether the three constituent simple layers are in a direct (ABCABC ...) or reverse (ACBAC ...) order, respectively.

Given that there are six kinds of layer (whose ordered list is α, α', β, β', γ, γ') six continuing probabilities are needed.

First, we take into account the stacking sequences that are experimentally most relevant, namely the stacking sequences corresponding to the polytypes most frequently found in the MX_2 compounds structurally related to $Ca(OH)_2$. The indefinite repetition of the sequences $\alpha \to \gamma'$, $\alpha \to \beta$ and $\alpha \to \alpha$ corresponds to the regular structure of polytypes 4H, 6R and 2H, respectively (see Figure 1). The corresponding probabilities will be denoted in the following with the letters a, b and c. The experimental patterns show that a c value close to one should be always considered.

In the assumption that an influence exists only between nearest layers, the same probability of sequence $\alpha \to \gamma'$ will be given to sequence $\alpha \to \beta'$, because the latter contains the reverse sequence of layers, merely relabelled.

Finally, sequences $\alpha \to \alpha'$ and $\alpha \to \gamma$ describe arrangements of anionic layers which are not close packed, so that the neglecting of their probabilities seems justified.

Now, the relevant matrices are

$$\boldsymbol{v} = \begin{pmatrix} A & B \\ C & D \end{pmatrix} \tag{20}$$

with

$$A = V(\alpha)\, V^*(\alpha)\,,$$
$$B = V(\alpha)\, V^*(\alpha') = C^*\,,$$
$$D = V(\alpha')\, V^*(\alpha')\,;$$

$$^1\boldsymbol{p} = \begin{pmatrix} c & 0 \\ 0 & c \end{pmatrix}, \quad ^2\boldsymbol{p} = \begin{pmatrix} b & a \\ a & 0 \end{pmatrix}, \tag{21), (22}$$

and

$$^3\boldsymbol{p} = \begin{pmatrix} 0 & a \\ a & b \end{pmatrix}, \tag{23}$$

so that (18) can be easily evaluated for arbitrary values of the h and k Miller indexes, of the number of layers (N) and of the stacking sequences probabilities (a, b and c, with $2a + b + c = 1$).

Figures 2–6 show the results obtained* with some representative values of the pertinent parameters (but always with c close to one).

According to the present approach, powder X-ray diffraction patterns (XRD) taken on small-sized and faulted particles of calcium hydroxide ought to show the following distinctive features:

a) $(h\,h\,0)$ lines are not affected by layer disorder; the same holds for $h\,k\,0$ lines if $(h-k) \bmod 3 = 0$;
b) broadening of $(0\,0\,l)$ lines occurs only in connection with small numbers of layers (N);
c) $(h\,k\,l)$ lines, with $(h-k) \bmod 3 \neq 0$, are broadened by all kinds of layer disorder (the broadening increases with increasing l), and peak asymmetry and displacement are expected when the stacking fault probability b is large;
d) layer disorder gives a significant contribution to diffuse scattering between Bragg peaks.

Actually, these results can be positively compared with the powder patterns of calcium hydroxide samples, if due allowance is made both for the complexity of the microstructural disorder of these materials and for its relevant dependence on the experimental procedures.

Indeed, several experimental techniques [3, 13, 14] have supplied evidence for the fact that calcium

* The numerical computations have been made with the values $a_0 = 0.358$ nm, and $c_0 = 0.490$ nm for the lattice constants of $Ca(OH)_2$, and $z = 0.23$ for the coordinate of the 0 atoms. The atomic scattering factors have been calculated with the interpolating formulae given by the International Tables [12] for Ca^{++} and O^- ions, and neglecting the anomalous dispersion.

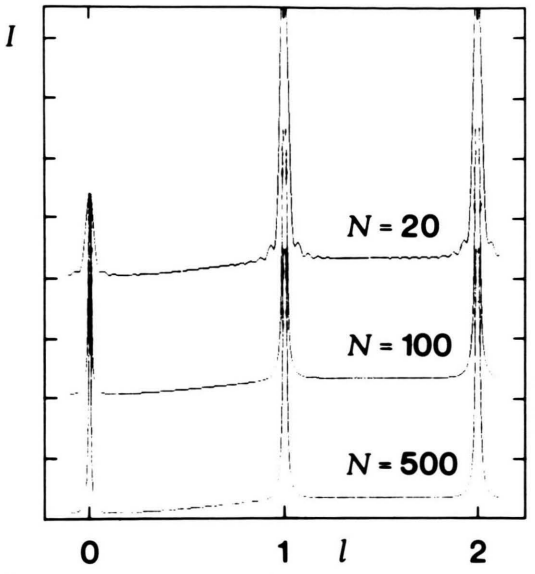

Fig. 2. Scattering intensity along the (1 0 l) line of the reciprocal lattice of a $Ca(OH)_2$ crystal with $a = 0.01$, $b = 0$ and with different thicknesses (N).

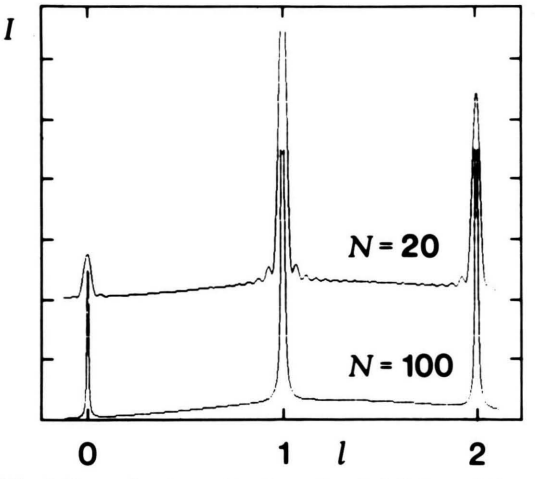

Fig. 3. Scattering intensity along the (1 0 l) line of the reciprocal lattice of a $Ca(OH)_2$ crystal with $a = 0$, $b = 0.01$ and with different thicknesses (N).

Fig. 6. Scattering intensity along the (1 0 l) and (2 0 l) lines of the reciprocal lattice of a $Ca(OH)_2$ crystal with $N = 20$, $a = 0$ and $b = 0.1$. The intensity scale is twice that of the previous Figures.

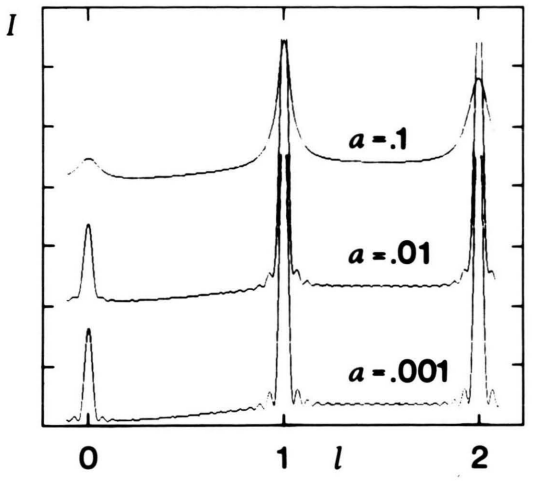

Fig. 4. Scattering intensity along the (1 0 l) line of the reciprocal lattice of a $Ca(OH)_2$ crystal with $N = 20$, $b = 0$ and with different a values.

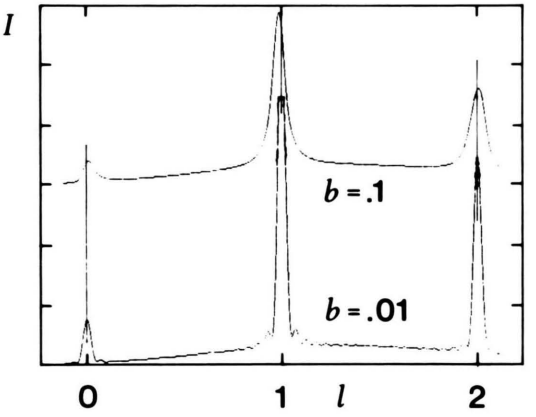

Fig. 5. Scattering intensity along the (1 0 l) line of the reciprocal lattice of a $Ca(OH)_2$) crystal with $N = 20$, $a = 0$ and with different b values.

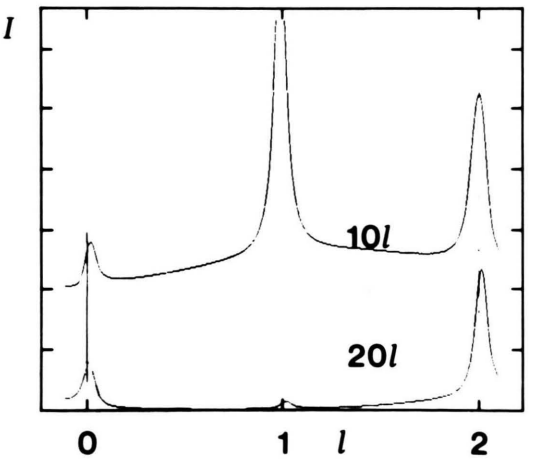

Table 1. Line breadth parameters of different calcium hydroxides.

h k l	Samples					
	A	B	Diff.%	C	D	Diff.%
0 0 1	0.54	0.38	30	0.69	0.42	40
1 0 0	0.30	0.12	60	0.41	0.12	70
1 0 1	0.72	0.33	54	1.10	0.55	50
1 0 2	0.97	0.49	50	1.43	1.08	25
1 1 0	0.39	0.24	40	0.46	0.35	24
1 1 1	0.50	0.31	38	0.93	0.55	40

Table 1. Line breadth parameters of different calcium hydroxides. A: calcium hydroxide produced from large CaO crystallites. B: same sample as A, but after thermal treatment. C: calcium hydroxide produced from small CaO crystallites. D: same sample as C, but after thermal treatment.

hydroxides with different microstructural properties can be produced when different starting materials or different working conditions are employed.

Table 1 reports the XRD line breadth parameters ($B \cos \vartheta$, B = line width at half height, corrected for instrumental broadening) of the powder patterns taken on two samples prepared through the reaction sequence calcium hydroxide → calcium oxide → calcium hydroxide. The hydration step was always carried out under highly irreversible conditions (so that poorly crystalline hydroxides were produced): the difference was in the nature of the intermediate oxides. In one case, the small-sized CaO particles produced in the decomposition step were directly hydrated; in the other case, before hydration, they were heated at 1100 K for several days, a treatment which produces larger CaO crystallites. Moreover, both hydroxide samples undergo an exothermal irreversible transformation to more crystalline materials when heated under a dry and decarbonated atmosphere, so that we were able to record four distinct powder XRD patterns*.

From an inspection of Table 1 we can gain evidence of monodimensional disorder by noting the values of the (1 0 *l*) lines, their trend with increasing *l*, and the values of the (0 0 1) and (1 1 0) lines. Moreover, a closer look at the patterns taken before the thermal treatment shows that there are measurable peak displacements for (1 0 *l*) lines, that their dependence on the *l* index is as expected, and that they almost disappear after the thermal treatment. It should be noted, however, that the above discussed model does not fully explain the microstructure of calcium hydroxides produced by vapour phase hydration: in particular, the large breadths of the (1 1 0) and (1 1 1) lines indicate that there is also a finite coherence size along the plane of the layers.

It is important to compare the results on the same sample before and after the thermal treatment. Quite clearly, during the irreversible transformation, a crystallite growth takes place, but this seems to be closely connected with (and possibly driven by) a recovery of stacking disorder.

A sistematic work is in progress to understand the rather complex influence of the experimental conditions on the microstructural disorder of the products of vapour phase hydration and on its recovery process: it is worth noting here that the picture so far obtained is in agreement with previous nitrogen adsorption isotherm and differential scanning calorimetry measurements [3, 13, 14].

* Apparatus and experimental procedures have been detailed previously [3].

[1] D. Beruto and A. W. Searcy, Nature London **263,** 221 (1976).
[2] B. E. Warren, X-ray Diffraction, Addison Wesley Publ. Co., Reading, 1969.
[3] D. Beruto, G. Spinolo, L. Barco, U. Anselmi Tamburini, and G. Belleri, Ceramics International **9,** 22 (1983).
[4] S. Hendricks and E. Teller, J. Chem. Phys. **10,** 147 (1942).
[5] A. J. C. Wilson, Proc. Roy. Soc. London **181,** 360 (1943).
[6] H. Jagodzinski, Acta Cryst. **7,** 17 (1954).
[7] G. Allegra, Acta Cryst. **17,** 579 (1964).
[8] J. Kakinoki and Y. Komura, Acta Cryst. **19,** 137 (1965).
[9] J. Kakinoki, Acta Cryst. **23,** 875 (1967).
[10] R. W. G. Wyckoff, Crystal Structures, Interscience Publ. Co., J. Wiley & Sons, New York 1963.
[11] G. C. Trigunayat and A. R. Verma, "Polytypism and Stacking Faults in Crystals with Layer Structures", in "Crystallography and Crystal Chemistry of Materials with Layered Structure", F. Levy ed., D. Reidel Publ. Co., Dordrecht, Holland, 1976.
[12] International Tables for X-Ray Crystallography, Vol. IV, Kynoch, Birmingham 1974.
[13] G. Spinolo and U. Anselmi Tamburini, Communication presented at the 4th Meeting of the Italian Association of Calorimetry and Thermal Analysis (A.I.C.A.T.), Catania 1982.
[14] D. Beruto, A. W. Searcy, L. Barco, and G. Belleri, 9th Intern. Symp. Reactivity of Solids, Cracow 1980.