FERROELASTICITY AND FERROELASTIC TRANSFORMATIONS (*)

D. M. C. GUIMARÃES
Department of Physics of Aveiro University
3800 AVEIRO — Portugal

(Received 28 October 1981)

ABSTRACT — Ferroelastic transformations can be calculated, when an n-fold pseudo-rotation exists (the n-fold rotation being a symmetry element of the prototype lost in the lower symmetry ferroelastic phase), by means of a transformation (rotation of axes) corresponding to the reorientation of the lattice vectors if distortion of the ferroelastic structure is taken into account.

1 — FERROELASTICITY

Ferroelasticity was recognized in 1969 as a new crystal property by K. Aizu [1]. A crystal is ferroelastic if it possesses two or more equally stable orientational states which differ in spontaneous strain, and if a suitably applied external mechanical stress can reproducibly transform one of these states into the others. Spontaneous strain is measured in relation to the prototype structure. The crystal symmetry is reduced, in the ferroelastic state, to a subgroup of a higher symmetry class (corresponding to the prototype structure) by a small distortion. The classification of potentially ferroelastic materials (from the point of view of symmetry) was developped by Aizu [2].

We discuss here the relation between the property of ferroelasticity and the crystal structure i.e. the incidence of this on the phenomenon of lattice reorientation under the effect of mechanical stress. As examples of the concepts in question we use samarium orthoaluminate, $Sm\ Al\ O_3$, and lead orthophosphate, $Pb_3\ (PO_4)_2$.

(*) Presented at the VII Iberoamerican Congress of Crystallography (21-26 September 1981, Coimbra, Portugal).

2 — FERROELASTICITY AND STRUCTURE IN SAMARIUM ORTHOALUMINATE

2.1 — *Description of the structure*

Crystals of $Sm\,Al\,O_3$ grow in a ferroelastic phase (Abrahams et al., [3]) whose structure corresponds to an hettotype of the perovskite family (Megaw, [4]).

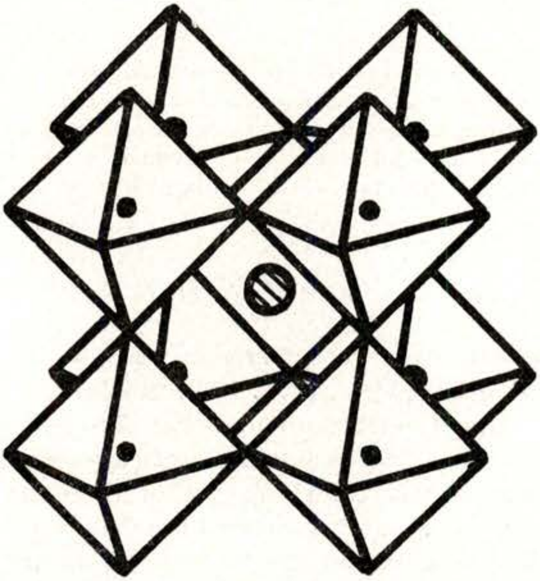

Fig. 1 — Ideal perovskite structure, ABO_3. Perspective view of the lattice, showing the octahedra: full circles B, hatched circle A, O atoms at the corners of the octahedra.

Fig. 1 shows the ideal perovskite structure. The general formula is $A\,B\,O_3$ (A and B are cations) and the lattice is primitive cubic. The structure can be simply described as a framework of $B\,O_6$ octahedra sharing corners, with the large A atom in the cavity between octahedra. This is the aristotype of the perovskite family. Note that the general formula of this family is $A\,B\,X_3$, in analogy with $A\,B\,O_3$, X being an anion.

The prototype structure of Sm Al O_3 is also an hettotype of the perovskite family. In this case the group O_6 around the Al cation becomes a tetragonal bipyramid instead of an octahedron; the point group in this ideal structure is 4/m m m.

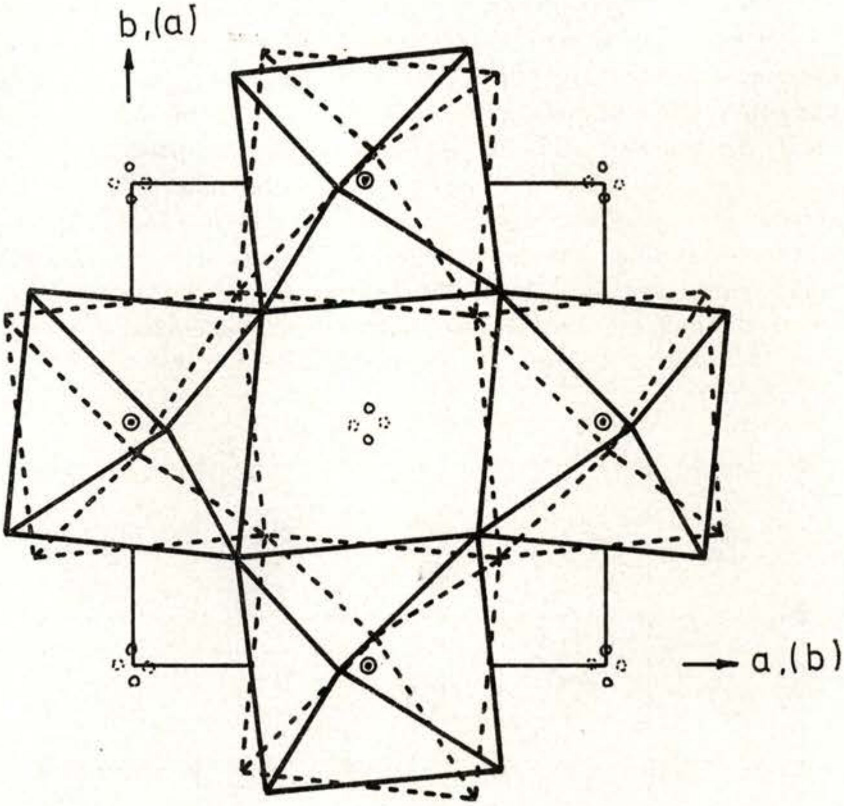

Fig. 2 — Atomic positions in Sm Al O_3, in initial *a b c* orientation (solid outlines) and in orientation *b a c* after ferroelastic transformation (dashed outlines). (from Abrahams et al., [3]).

In the real ferroelastic phase the groups Al O_6 tilt relative to one another; the distortion may occur in two different ways which correspond to two well determined orientations of the crystal lattice. The point group is m m m. The two stable states are energetically equivalent and only distinguishable by their orientation in space. Fig. 2 shows the atomic positions in both orientation states. In this example, the ferroelastic phase is orthorhombic, pseudo-tetragonal. By means of an adequate compressive stress along the [100] or [010] crystallographic directions, small atomic movements occur (of the order of tenths of Å) which give rise to ferroelastic switching from one state to the other. The phenomenon is clearly observed in polarized light.

Point group m m m is a subgroup of 4/m m m. Besides all symmetry elements of the ferroelastic structure, the prototype has other symmetry elements, such as rotations by $\pi/2$ and $3\pi/2$ about the fourfold axis. These rotations, when applied to one of the ferroelastic states transform it into the other. There is a geometric correspondence between the stable ferroelastic states that is established by the symmetry elements of the prototype which have been lost in the ferroelastic phase.

Fig. 3 indicates in a diagram (taken down the c axial direction) how the axes in the prototype are chosen in order to refer to them the distortion of the ferroelastic phase. It is seen (the axial length *c* duplicates) that there is a quadruplication of the unit cell in the ferroelastic phase.

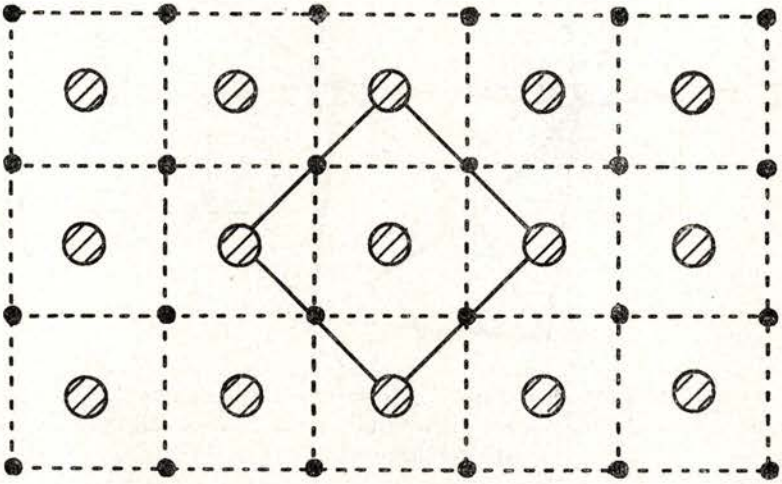

Fig. 3 — Choice of axes in the prototype, coincident with the axes in the ferroelastic phase of Sm Al O_3. [Projection in (001)].

The preparation of the crystals, lattice constants and atomic coordinates in samarium orthoaluminate are described by Abrahams et al., [3]. We give here the indispensable data for the analysis of the ferroelastic transformation that is dealt with in section 2.2.

The lattice constants are

$$a = 5.291075 \pm 0.000024 \text{ Å}$$
$$b = 5.290479 \pm 0.000024 \text{ Å}$$
$$c = 7.474200 \pm 0.000051 \text{ Å}$$

2.2 — *Ferroelastic transformation in samarium orthoaluminate*

According to a well known criterion about the structural basis of ferroelasticity (Abrahams et al., [5]) — this criterion being applicable only when two possible ferroelastic domains are in question — every atom in Sm Al O_3 at x_1, y_1, z_1 is pseudo-symmetrically related to another atom of the same kind, with coordinates x_2, y_2, z_2, by the equation

$$x_1, y_1, z_1 = (1/2 - y_2, 1/2 - x_2, 1/2 + z_2) + \Delta \qquad (1)$$

where Δ is an atomic displacement of the order of tenths of Å.

On the basis of the transformation relation (1), Abrahams et al. calculate the coordinates of every atom, after the ferroelastic switching to the other orientational state (the axes of reference being the initial ones) as well as the atomic displacements Δ that take place in the transformation.

Considering the symmetry relations between the prototype and the ferroelastic phase we do here the same determinations and obtain the same results. This method is quite general, since ferroelastic transformations can be carried out in this way also in the case of more than two ferroelastic domains.

Let us refer the prototype structure to the axes of the ferroelastic phase which is a small distortion of the first. Having in mind one of the ferroelastic states, let us rotate the lattice by $\pi/2$ around the c^* axis direction (pseudo-fourfold axis). Supposing the domains related by fourfold clockwise rotation, the axes for the transformation of coordinates must be correspondingly rotated anti-clockwise.

If the axes *a* and *b* are considered of equal length, the simple transformation of coordinates (x′, y′, z′ are the coordinates in domain 2 referred to the original axes of domain 1) is

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} \tag{2}$$

Note that ratio a/b is different from 1. From a geometric point of view, the exact transformation of coordinates would be

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} 0 & b/a & 0 \\ -a/b & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} \tag{3}$$

The use of (2) instead of (3) doesn't really alter the results, due to the precision with which the atomic coordinates are known. This is not the case of ferroelastic transformations in other materials, such as $Pb_3(PO_4)_2$, to which we refer further on.

When relations of type (1) are used, simplifications similar to the one we have emphasized here are implicit.

The ferroelastic transformation in Sm Al O_3, obtained by use of the method we have just outlined, is detailed in Table 1. The first column of this Table indicates the identity of the atom in the ferroelastic state 1 whose position in ferroelastic state 2 one wants to determine by means of relations (2); its coordinates are given in the second column. The third column gives the identity of the atom (Atom*) which must be considered to obtain the required ferroelastic transformation. In the fourth column the coordinates of Atom* are given; and in the fifth those of the particular Atom* to be chosen to carry out transformation (2) (x, y, z coordinates). In the sixth column the result of the ferroelastic transformation is written and in the seventh the atomic displacement undergone by the initial atom. *The reference axes remain those that have been initially chosen in ferroelastic state 1*. In the transformed lattice, the identity of the atom after the ferroelastic transformation is the same as Atom*. Note that, in the prototype, coordinates x′, y′, z′ (result of the ferroelastic transformation) coincide with the initial coordinates of the atom, denoted by XYZ in the second column of Table 1.

TABLE 1 — Atomic coordinates and displacement vectores Δ in ferroelastic transformation of Sm Al O_3

Atom	Coordinates	Atom*	Coordinates	Coordinates*	Result	Δ (Å)
Sm-1	X = — 0.00501	Sm-1	X′ = — 0.00501	x = — 0.00501	x′ = 0.02402	0.184
	Y = 0.02402		Y′ = 0.02402	y = 0.02402	y′ = 0.00501	
	Z = 1/4		Z′ = 1/4	z = 1/4	z′ = 1/4	
Sm-2	X = 0.00501	Sm-2	X′ = 0.00501	x = 0.00501	x′ = — 0.02402	0.184
	Y = — 0.02402		Y′ = — 0.02402	y = — 0.02402	y′ = — 0.00501	
	Z = 3/4		Z′ = 3/4	z = 3/4	z′ = 3/4	
Sm-3	X = 0.49499	Sm-3	X′ = 0.49499	x = — 0.50501	x′ = 0.47598	0.184
	Y = 0.47598		Y′ = 0.47598	y = 0.47598	y′ = 0.50501	
	Z = 3/4		Z′ = 3/4	z = 3/4	z′ = 3/4	
Sm-4	X = 0.50501	Sm-4	X′ = 0.50501	x = — 0.49499	x′ = 0.52402	0.184
	Y = 0.52402		Y′ = 0.52402	y = 0.52402	y′ = 0.49499	
	Z = 1/4		Z′ = 1/4	z = 1/4	z′ = 1/4	
Al-1	X = 0	Al-2	X′ = 1/2	x = — 1/2	x′ = 0	0
	Y = 1/2		Y′ = 0	y = 0	y′ = 1/2	
	Z = 0		Z′ = 0	z = 0	z′ = 0	
Al-2	X = 1/2	Al-1	X′ = 0	x = 0	x′ = 1/2	0
	Y = 0		Y′ = 1/2	y = 1/2	y′ = 0	
	Z = 0		Z′ = 0	z = 0	z′ = 0	
Al-3	X = 1/2	Al-4	X′ = 0	x = 0	x′ = 1/2	0
	Y = 0		Y′ = 1/2	y = 1/2	y′ = 0	
	Z = 1/2		Z′ = 1/2	z = 1/2	z′ = 1/2	

TABLE 1 — (continuation)

Atom	Coordinates	Atom*	Coordinates	Coordinates*	Result	Δ (Å)
Al-4	X = 0 Y = 1/2 Z = 1/2	Al-3	X′ = 1/2 Y′ = 0 Z′ = 1/2	x = − 1/2 y = 0 z = 1/2	x′ = 0 y′ = 1/2 z′ = 1/2	0
0 (1)-1	X = 0.0644 Y = 0.4903 Z = 1/4	0 (1)-4	X′ = 0.4356 Y′ = 0.9903 Z′ = 1/4	x = − 0.5644 y = − 0.0097 z = 1/4	x′ = − 0.0097 y′ = 0.5644 z′ = 1/4	0.554
0 (1)-2	X = − 0.0644 Y = 0.5097 Z = 3/4	0 (1)-3	X′ = 0.5644 Y′ = 0.0097 Z′ = 3/4	x = − 0.4356 y = 0.0097 z = 3/4	x′ = 0.0097 y′ = 0.4356 z′ = 3/4	0.554
0 (1)-3	X = 0.5644 Y = 0.0097 Z = 3/4	0 (1)-2	X′ = − 0.0644 Y′ = 0.5097 Z′ = 3/4	x = − 0.0644 y = 0.5097 z = 3/4	x′ = 0.5097 y′ = 0.0644 z′ = 3/4	0.409
0 (1)-4	X = 0.4356 Y = 0.9903 Z = 1/4	0 (1)-1	X′ = 0.0644 Y′ = 0.4903 Z′ = 1/4	x = 0.0644 y = 0.4903 z = 1/4	x′ = 0.4903 y′ = − 0.0644 z′ = 1/4	0.409
0 (2)-1	X = − 0.2766 Y = 0.2770 Z = 0.0335	0 (2)-8	X′ = 0.7766 Y′ = 0.7770 Z′ = 0.0335	x = − 0.2234 y = − 0.2230 z = 0.0335	x′ = − 0.2230 y′ = 0.2234 z′ = 0.0335	0.401
0 (2)-2	X = 0.7766 Y = 0.7770 Z = 0.4665	0 (2)-3	X′ = 0.2766 Y′ = − 0.2770 Z′ = 0.5335	x = − 0.7234 y = 0.7230 z = 0.5335	x′ = 0.7230 y′ = 0.7234 z′ = 0.5335	0.642

TABLE 1 — (continuation)

Atom	Coordinates	Atom*	Coordinates	Coordinates*	Result	Δ (Å)
0 (2)-3	X = 0.2766 Y = −0.2770 Z = 0.5335	0 (2)-6	X′ = 0.2234 Y′ = 0.2230 Z′ = 0.5335	x = 0.2234 y = 0.2230 z = 0.5335	x′ = 0.2230 y′ = −0.2234 z′ = 0.5335	0.401
0 (2)-4	X = 0.2234 Y = 0.2230 Z = −0.0335	0 (2)-1	X′ = −0.2766 Y′ = 0.2770 Z′ = 0.0335	x = −0.2766 y = 0.2770 z = 0.0335	x′ = 0.2770 y′ = 0.2766 z′ = 0.0335	0.642
0 (2)-5	X = 0.2766 Y = −0.2770 Z = −0.0335	0 (2)-4	X′ = 0.2234 Y′ = 0.2230 Z′ = −0.0335	x = 0.2234 y = 0.2230 z = −0.0335	x′ = 0.2230 y′ = −0.2234 z′ = −0.0335	0.401
0 (2)-6	X = 0.2234 Y = 0.2230 Z = 0.5335	0 (2)-7	X′ = −0.2766 Y′ = 0.2770 Z′ = 0.4665	x = −0.2766 y = 0.2770 z = 0.4665	x′ = 0.2770 y′ = 0.2766 z′ = 0.4665	0.642
0 (2)-7	X = −0.2766 Y = 0.2770 Z = 0.4665	0 (2)-2	X′ = 0.7766 Y′ = 0.7770 Z′ = 0.4665	x = −0.2234 y = −0.2230 z = 0.4665	x′ = −0.2230 y′ = 0.2234 z′ = 0.4665	0.401
0 (2)-8	X = 0.7766 Y = 0.7770 Z = 0.0335	0 (2)-5	X′ = 0.2766 Y′ = −0.2770 Z′ = −0.0335	x = −0.7234 y = 0.7230 z = −0.0335	x′ = 0.7230 y′ = 0.7234 z′ = −0.0335	0.642

In short, if atoms with coordinates XYZ and xyz are independent crystallographic atoms of the same kind, we can write

$$(XYZ) = R\ (xyz) + \Delta \qquad (4)$$

where R (xyz) is a transformation (a clockwise rotation of the lattice by $\theta = \pi/2$ around the pseudo-fourfold axis) that causes reorientation of the lattice vectors; Δ is an atomic displacement of the order of tenths of Å and represents the effective displacement of the atom with coordinates XYZ in the process of ferroelastic switching from one domain to the other.

An atom that is situated on the fourfold axis in the prototype, may occur in the ferroelastic phase in one of two possible positions (according to the domain it is in) that are symmetrically placed around the pseudo-fourfold axis:

XYZ – domain 1 ; R (XYZ) – domain 2.

3 — FERROELASTICITY AND STRUCTURE IN LEAD ORTHOPHOSPHATE

In lead orthophosphate, $Pb_3(PO_4)_2$, there are in general triplets of crystallographically-independent atoms of the same kind that are pseudo-symmetrically related by a pseudo-threefold rotation (Guimarães, [6]).

The material undergoes a phase transition to a high temperature phase at about 180 C.

3.1 — *Structure and ferroelastic domains in lead orthophosphate*

The high and low temperature structures are fully described in the literature. Fig. 4 shows the stereogram of the symmetry change.

The high temperature phase (prototypic phase or β phase) whose structure is rhombohedral (point group $\bar{3}$m) may be referred to the monoclinic axes of the low temperature phase (ferroelastic phase or α phase, point group $2/m$) and this is convenient for the study of spontaneous strain (Guimarães, [7]) and ferroelastic transformations.

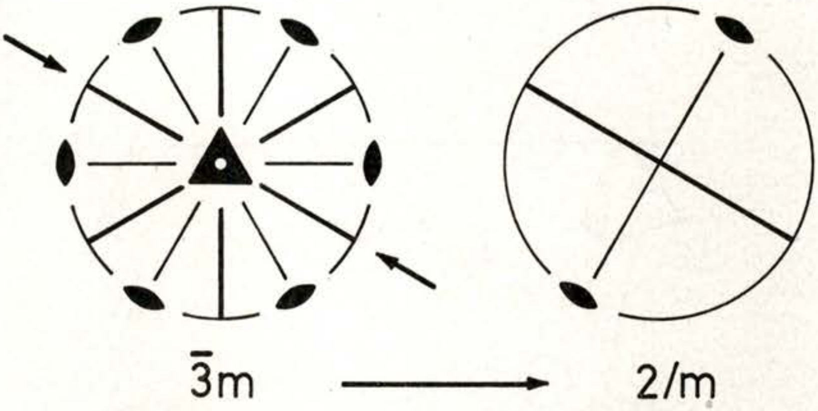

Fig. 4 — Stereogram of the symmetry change in the phase transition of $Pb_3(PO_4)_2$.

The projection of the ferroelastic structure on the monoclinic (010) plane is shown in Fig. 5. The pseudo-threefold axis is along a_m^* and passes through the point (0 , 1/4 , 1/4) with respect to the centre of symmetry.

There are in the α phase three possible orientations of ferroelastic domains, related to one another by a threefold rotation about the pseudo-threefold axis.

3.2 — *Ferroelastic transformations in lead orthophosphate*

The real monoclinic ferroelastic lattice is slightly distorted in relation to the monoclinic ideal sub-lattice of the rhombohedral β phase.

$Pb_3(PO_4)_2$ was the first example of a ferroelastic material with more than two domains where it was possible to find a structural explanation of the ferroelastic properties and to set up a scheme for the achievement of ferroelastic transformations.

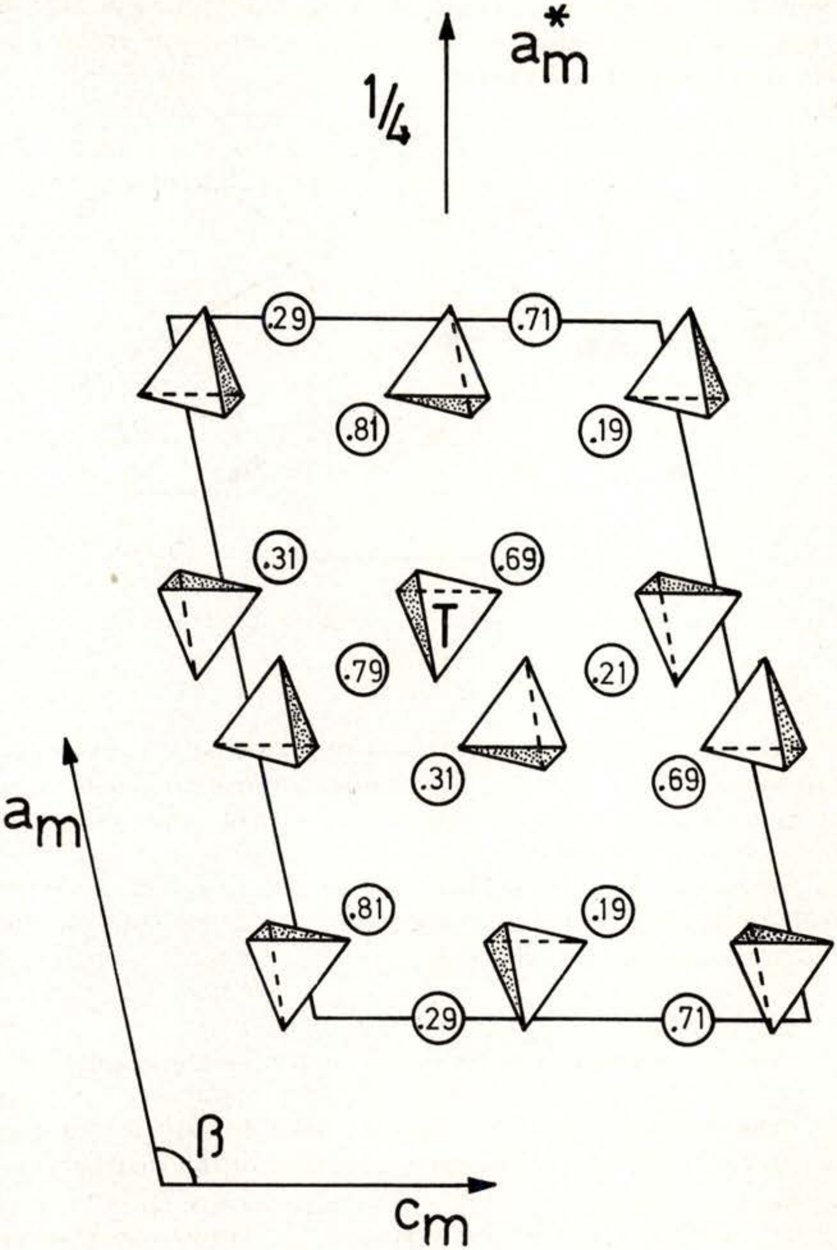

Fig. 5 — Projection of the $Pb_3(PO_4)_2$ ferroelastic structure on the (010) monoclinic plane (origin on centre of symmetry). The y coordinates are given inside the circles.

This method has proved to be general and includes the materials studied previously, with two domains only.

Atomic coordinates are denoted x^1, y^1, z^1 in domain 1 ; x^2, y^2, z^2 in domain 2 ; and x^3, y^3, z^3 in domain 3 (Guimarães, [6]). To obtain coordinates in domains 2 and 3, the lattice is rotated by $2\pi/3$ and $2 \times 2\pi/3$, respectively, about the reciprocal a_m^* axis that is common to the three domains (pseudo-threefold axis). The domains are considered in this case disposed around a_m^* anti-clockwisely, and the rotations of axes for the transformations of coordinates are, accordingly, clockwise.

The result is the following $(u = c_m/b_m)$:

$$\begin{bmatrix} x^2 \\ y^2 \\ z^2 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ \frac{\sqrt{3}}{2}\, u\, \frac{a_m}{c_m} \cos\beta & -\frac{1}{2} & \frac{\sqrt{3}}{2}\, u \\ -\frac{3}{2}\, \frac{a_m}{c_m} \cos\beta & -\frac{\sqrt{3}}{2} \cdot \frac{1}{u} & -\frac{1}{2} \end{bmatrix} \begin{bmatrix} x^1 \\ y^1 \\ z^1 \end{bmatrix} \tag{5}$$

and

$$\begin{bmatrix} x^3 \\ y^3 \\ z^3 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ -\frac{\sqrt{3}}{2}\, u\, \frac{a_m}{c_m} \cos\beta & -\frac{1}{2} & -\frac{\sqrt{3}}{2}\, u \\ -\frac{3}{2}\, \frac{a_m}{c_m} \cos\beta & \frac{\sqrt{3}}{2} \cdot \frac{1}{u} & -\frac{1}{2} \end{bmatrix} \begin{bmatrix} x^1 \\ y^1 \\ z^1 \end{bmatrix} \tag{6}$$

In the high temperature phase $(a_m/c_m) \cos\beta = -1/3$ and the quantity u is equal to $\sqrt{3}$. Matrices (5) and (6) include the transformation matrices that are obtained when the ferroelastic distortion is absent and take into account the distortion present when the structure is in its low-temperature modification. By adequate use of (5) and (6) the transformed coordinates in domains 2 and 3 are obtained, *axes of reference being those chosen for domain 1.*

We make here only a short reference to the use of the method. Consider the PO_4 tetrahedron marked T in Fig. 5.

Atoms 0(1), 0(2) and 0(3), which form this tetrahedron with P and 0(4) almost aligned along the pseudo-threefold axis, are crystallographically independent in the α phase; they are pseudosymmetrically related by the pseudo-threefold rotation and interchange identity in the ferroelastic transformations. Note that although we are relating two atomic positions by a rotation, we emphasize that the *actual* movement of the atoms in question is only a small displacement.

REFERENCES

[1] K. AIZU, *J. Phys. Soc. Japan*, **27**, 387 (1969).

[2] K. AIZU, *Phys. Rev.* **B2**, 754 (1970).

[3] S. C. ABRAHAMS, J. L. BERNSTEIN and J. P. REMEIKA, *Mat. Res. Bull.*, **9**, 1613 (1974).

[4] H. D. MEGAW, *Crystal Structures: a Working Approach*, W. B. Saunders Company (1973).

[5] S. C. ABRAHAMS and E. T. KEVE, *Ferroelectrics*, **2**, 129 (1971).

[6] D. M. C. GUIMARÃES, *Acta Cryst.*, **A35**, 108 (1979).

[7] D. M. C. GUIMARÃES, *Phase Transitions*, **1**, 143 (1979).