SYMMETRY CONSTRAINTS ON THE PHYSICAL PROPERTIES OF AN ANISOTROPIC MATERIAL

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PURPOSE

This is not an original work.

It is a review of the constraints required

by the crystal symmetry

on the anisotropic properties of crystalline materials.

References

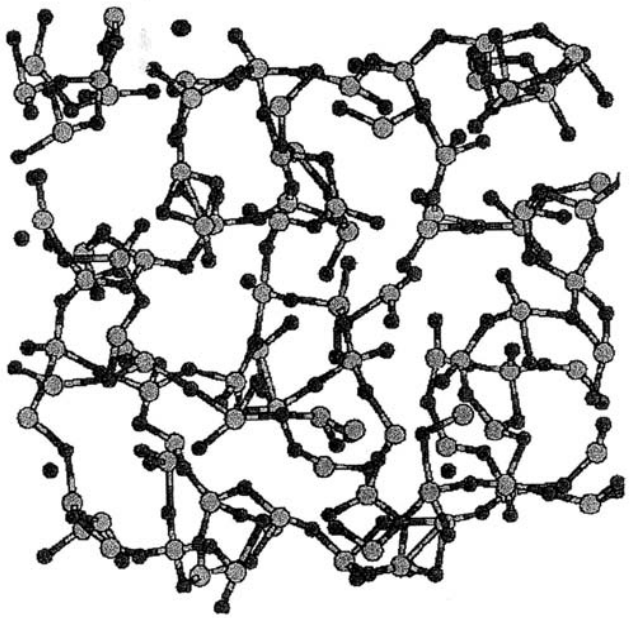
- A. Putnis – *Introduction to mineral sciences*. Cambridge 1992.
- M. Catti - *Physical properties of crystals*:

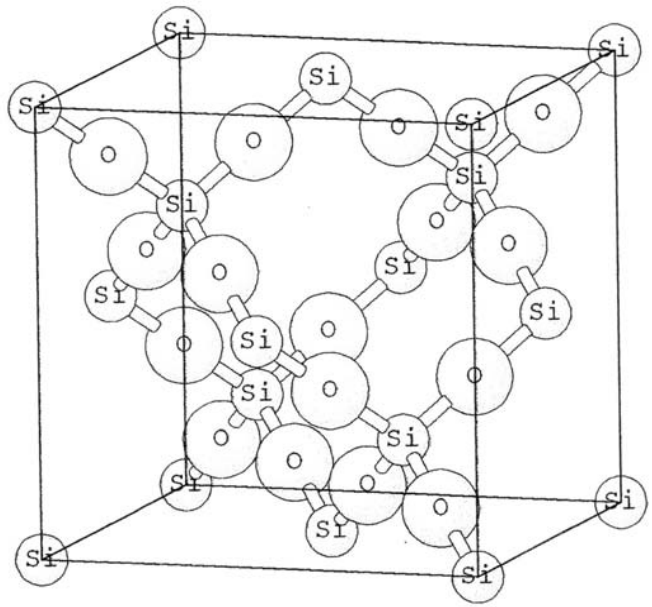
in C. Giacovazzo *et al. Fundamentals of Crystallography.* Oxford 2002.

- E. Hartmann – *An introduction to crystal physics*. IUCr website.
- D.R. Lowett – *Tensor properties of crystals.* Bristol 1999.

ANISOTROPY vs. ISOTROPY

Order vs. disorder

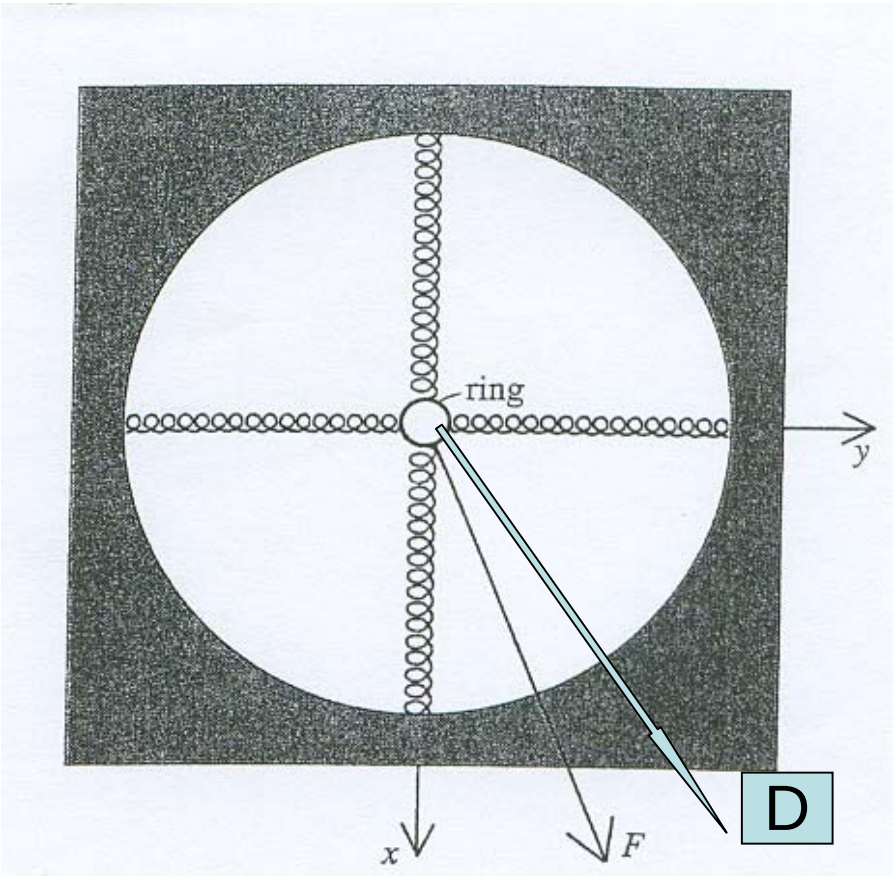




Silica glass
No long-range order of SiO_4 tetrahedra

Crystal structure of β-cristobalite
Long-range order of SiO_4 tetrahedra

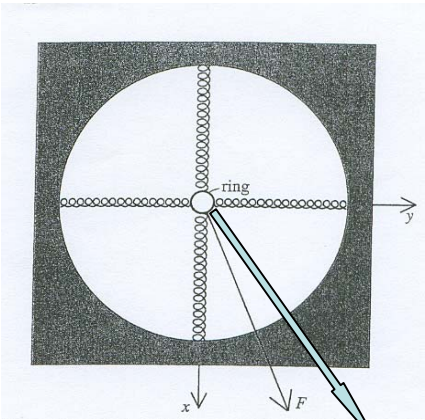
MECHANICAL ANALOGY



Along *x* and *y* the springs have different force constants. A force **F** (*cause* vector) displaces the ring along a direction **D** (*effect* vector) different from that of **F**, except when **F** is parallel either to the *x* or *y directions*.

IN GENERAL, IN AN ANISOTROPIC MEDIUM
A CAUSE ACTING ALONG A DIRECTION
GENERATES EFFECTS ALONG OTHER DIRECTIONS

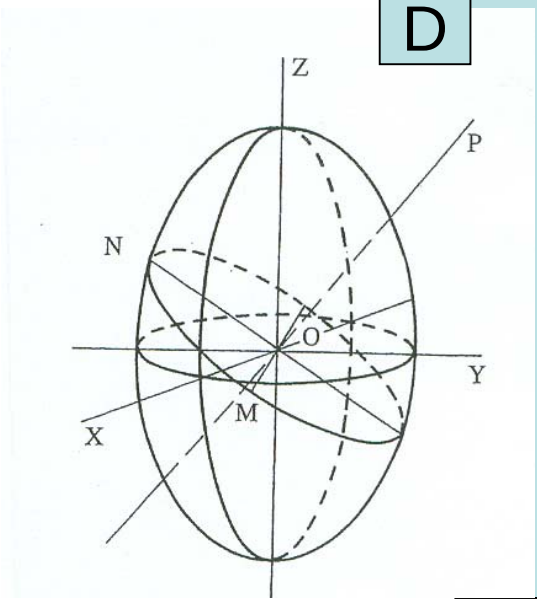
SURFACE DESCRIBED BY THE VECTOR D



D

Changing the direction of the *cause* vector **F**, the tip of the *effect* vector **D** describes an ellipsoid which is represented by the equation

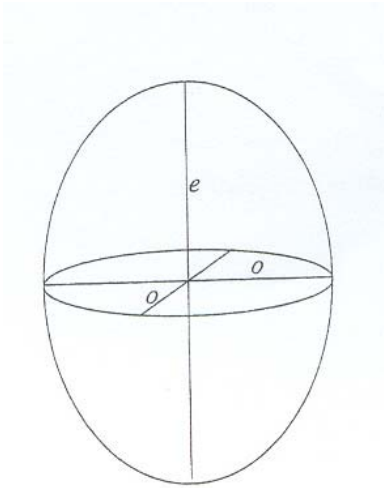
$$a_{11}x^2 + a_{22}y^2 + a_{33}z^2 + 2a_{12}xy + 2a_{13}xz + 2a_{23}yz = 1$$



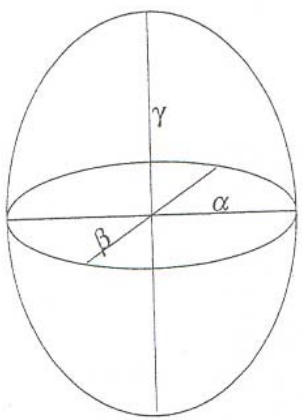
The a_{ij} coefficients are the elements of a matrix A.
The relationship between the cause vector **F** and the effect vector **D** is expressed as

D = A**F**

SYMMETRY CONSTRAINTS (1)



(a)



(b)

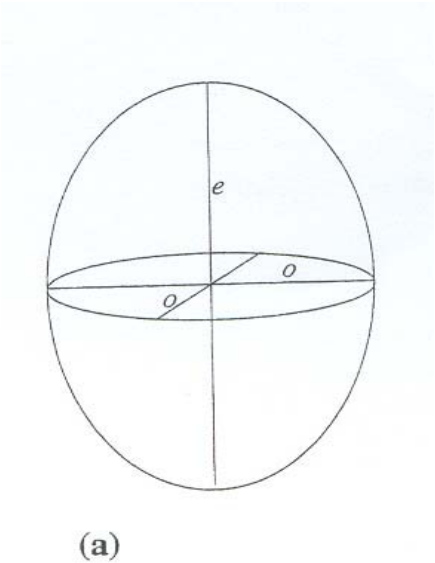
According to the Neumann principle, the symmetry of a physical property cannot be **lower than** that of the crystal point group.

A **general ellipsoid** (b) shows symmetry *mmm* which is compatible with triclinic (1, -1), monoclinic (2, *m*, 2/*m*) and orthorhombic (222, *mm2*, *mmm*) point groups.

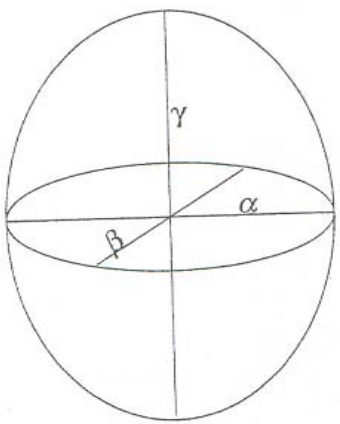
To be compatible with the presence of a rotation axis 3 (trigonal), 4 (tetragonal) or 6 (hexagonal), an ellipsoid is constraint to be a **rotation ellipsoid** (a) (symmetry ∞/m).

To be compatible with the presence of more than one rotation axis 3 (cubic), the ellipsoid is constrained to be a **sphere**.

SYMMETRY CONSTRAINTS (2)



(a)



(b)

Conditions to match ellipsoid and crystal symmetry

The rotation axis of the ellipsoid must be parallel to the rotation axis 3, 4, 6 of the crystal

The symmetry planes of the ellipsoid must coincide with symmetry planes of the crystal

In monoclinic crystals only the direction of one twofold axis of the ellipsoid is constrained; thus the ellipsoid can rotate around the constrained axis.

No orientation constraints in triclinic crystals.

SYMMETRY CONSTRAINTS (3)

Consequently to the symmetry constraints, the number of a_{ij} coefficients in the ellipsoid equation

$$a_{11}x^2 + a_{22}y^2 + a_{33}z^2 + 2a_{12}xy + 2a_{13}xz + 2a_{23}yz = 1$$

reduces and the corresponding matrix A assumes the following forms:

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ & a_{22} & a_{23} \\ & & a_{33} \end{pmatrix}$$
Triclinic

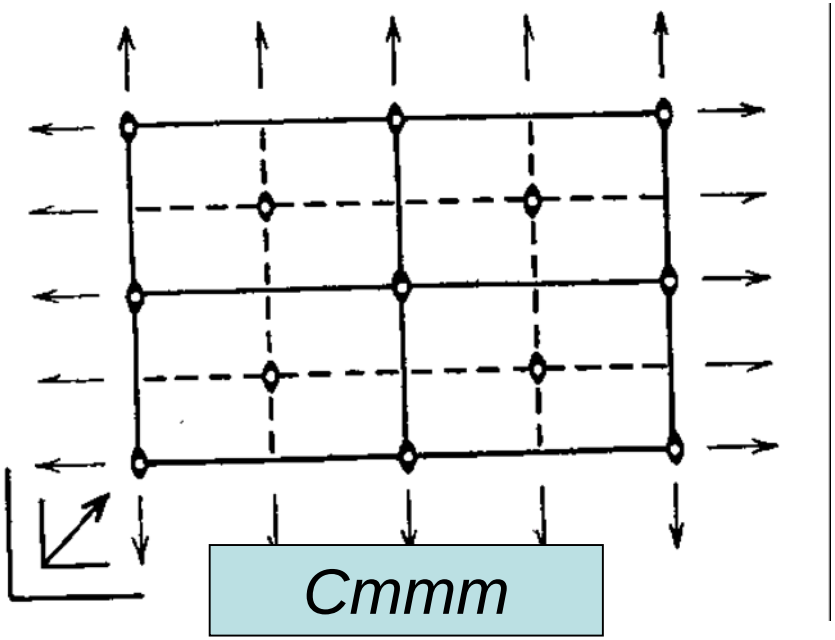
$$\begin{pmatrix} a_{11} & 0 & a_{13} \\ & a_{22} & 0 \\ & & a_{33} \end{pmatrix}$$
Monoclinic

$$\begin{pmatrix} a_{11} & 0 & 0 \\ & a_{22} & 0 \\ & & a_{33} \end{pmatrix}$$
Orthorhombic

$$\begin{pmatrix} a_{11} & 0 & 0 \\ & a_{11} & 0 \\ & & a_{33} \end{pmatrix}$$
Tetragonal, trigonal, hexagonal

$$\begin{pmatrix} a_{11} & 0 & 0 \\ & a_{11} & 0 \\ & & a_{11} \end{pmatrix}$$
Cubic

MICROSCOIC PHYSICAL PROPERTIES



If a physical property does not depend from a volume of matter (more unit cells), but is confined within one unit cell (i.e., refers to an atomic site), the symmetry is constrained not by the crystal point group, but by the site symmetry.

EXAMPLES

Atomic displacements and electronic deformation

Form and orientation of the thermal motion and electronic deformation are a function of the Wyckoff position..

TENSORIAL REPRESENTATION

The functional dependence between two vector physical properties **X** and **Y** can be expressed via a Taylor expansion:

$$Y = Y_0 + (dY/dX)_0 X + 1/2(d^2Y/dX^2)_0 X^2 + \ldots$$

If **X** (*cause*) and **Y** (*effect*) are not parallel, each of the three Cartesian components Y_i (i = 1,2,3) is a function of the three Cartesian components X_i. A Taylor expansion for each Y_i component is necessary

$$Y_i = Y_{0,i} + \Sigma_h(\partial Y_i/\partial X_h)_0 X_h + 1/2\Sigma_{h,k}(\partial^2 Y_i/\partial X_h \partial X_k)_0 X_h X_k + \ldots =$$
$$= Y_{0,i} + \Sigma_h a_{ih} X_h + \Sigma_{h,k} a_{ihk} X_h X_k + \ldots$$

TENSORS

Given

$$Y_i = Y_{0,i} + \Sigma_h a_{ih} X_h + \Sigma_{h,k} a_{ihk} X_h X_k + \ldots (i = 1,2,3)$$

the relationship between **Y** and **X** at the *n*th approximation is expressed by 3^{n+1} coefficients which are the components of a **tensor**.

$n + 1$ is the **rank** of the tensor.

The 0th approximation is a vector with components $Y_i = Y_{0,i}$: a vector represents a first-rank tensor.

By analogy, a scalar, which has only one component, is known as a zero-rank tensor.

COMPONENTS OF A TENSOR
Reduction inherent to the physical property

For the ellipsoid (second-rank tensor) describing the relationship between the displacement **D** and a force **F**, we have seen that the number of components $3^{1+1} = 9$ is reduced via two mechanisms.

Mechanism (1)

The surface described by **D** when the direction of **F** changes is an ellipsoid whose equation shows $a_{ij} = a_{ji}$, thus the nine components are reduced to six. This kind of tensors is said symmetrical second-rank tensor. **Not all second-rank tensors are symmetrical.**

COMPONENTS OF A TENSOR
Reduction inherent to the crystal symmetry

Mechanism (2)

The crystal symmetry requires equivalence between different directions within the crystal. Thus a lower number of components is necessary to fix the tensor. For the ellipsoid described by **D**, the six components of the general case (triclinic) are reduced to four (monoclinic), three (orthorhombic), two (tetragonal, trigonal, hexagonal), one (cubic).

PYROELECTRICITY

If a material shows a spontaneous polarization, in the Taylor expansion of the electric induction **D** as a function of an external electric field **E**

$$D_i = D_{0,i} + \Sigma_h \varepsilon_{ih} E_h + \Sigma_{h,k} \varepsilon_{ihk} E_h K_k + \ldots$$

the term $D_{0,i}$ (indicated as $P_{0,i}$ = polarization) is not null.

$P_{0,i} = D_{0,i}$ are the components of a vector (first-rank tensor).

The "spontaneous polarization" is only virtual, because opposite electrical charges recombine very fast.

Dipoles can however survive along polar directions whose extremes are kept at different temperatures.

PYROELECTRICITY AND SYMMETRY
Polar vectors

The pyroelectricity vector is a *polar vector*, i.e. a vector with symmetry ∞m.

The symmetry ∞m is compatible only with 10 acentric point groups: 1, 2, 3, 4, 6, *m*, *mm*2, 3*m*, 4*mm*, 6*mm*.

With point group 1, the dipole **P** can have any orientation and thus needs three components p_1, p_2, p_3.

With point group *m*, **P** must be parallel to the (010) plane, thus only p_1 and p_3 are not null.

With point group *2*, **P** must be parallel to the [010] direction, thus only p_2 is not null.

With crystal symmetry 3, 4, 6, *mm*2, 3*m*, 4*mm or* 6*mm*, **P** is parallel to the [001] direction, thus only p_3 is not null.

AXIAL VECTORS AND SYMMETRY

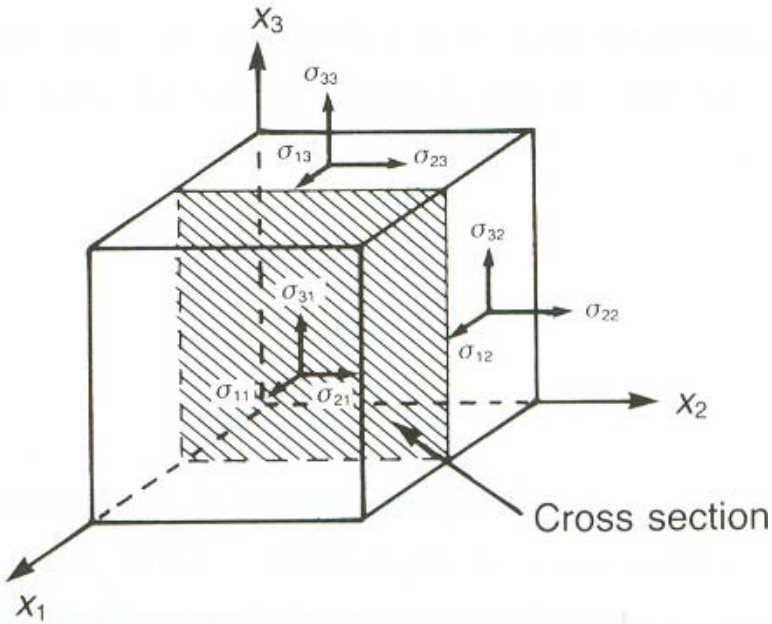
For some physical quantities it is necessary to define the direction of rotation: these properties must be represented by an ***axial tensor***.

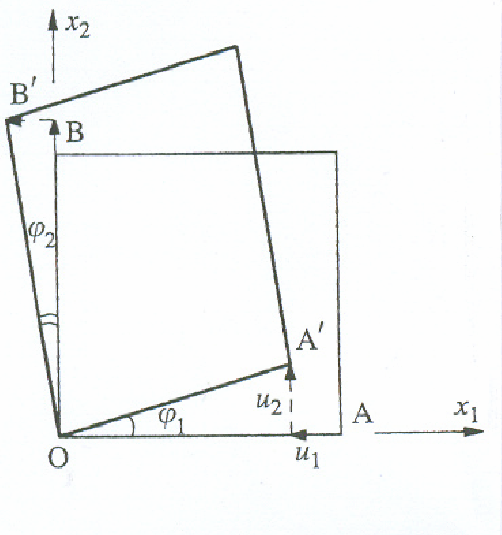
E,g., the angular velocity is an *axial vector* (first-rank axial tensor).

The symmetry of an axial vector is ∞/m; it is compatible only with 13 point groups:

1, -1, 2, *m*, 2/*m*, 3, -3, 4, -4, 6, -6, 4/*m*, 6/*m*.

STRESS and STRAIN





A *stress* is defined as a force per unit area. If a stress is applied to an anisotropic medium it acts differently in different directions and must be represented by a symmetric second-rank tensor σ_{hk}.

Under application of a stress, an anisotropic medium is differently deformed (strained) in different directions. The consequent *strain* (deformation) is represented by a symmetric second-rank tensor ε_{ij}.

PIEZOELECTRICITY

In 20 out of 21 acentric point groups (only 432 is excluded), the application of a stress σ_{hk} along a suitable direction generates an electric dipole **P**.

The relation between σ_{hk} and each component P_i of **P** is

$$P_i = \Sigma_{h,k} d_{ihk} \sigma_{hk}$$

d_{ihk} are the components of a **third-rank tensor** known as ***piezoelectric tensor***.

For a third-rank tensor d_{ihk} 27 components are expected. But σ_{hk} is symmetric, thus $d_{ihk} = d_{ikh}$ and the number of components reduces to 18 (triclinic crystals).

The crystal symmetry constrains the 18 components allowed in the triclinic crystals to: 10 or 8 (monoclinic); 9 (orthorhombic); 7 or 6 (tetragonal); 6, 4 or 2 (trigonal); 4, 2 or 1 (hexagonal); 1 (cubic).

ELASTICITY

The application of a stress σ_{hk} generates a strain ε_{ij}. The relationship between stress and strain is

$$\varepsilon_{ij} = s_{ijhk}\sigma_{hk}.$$

s_{ijhk} is a **fourth-rank tensor** known as *compliance tensor*; it represents the "easiness of deformation" of the medium.

The expected 81 s_{ijhk} components are reduced to 36 because

$$s_{ijhk} = s_{jihk} = s_{ijkh} = s_{jikh}$$

due to the symmetry of ε_{ij} and σ_{hk}

A further reduction from 36 to 21 components is obtained because it can be shown that

$$s_{ijhk} = s_{hkij}.$$

The crystal symmetry constrains the 21 components allowed in the triclinic crystals to: 13 (monoclinic); 9 (orthorhombic); 7 or 6 (tetragonal, trigonal); 4, 3 or 2 (hexagonal); 3 (cubic).

CONCLUSIONS

An **anisotropic property** is represented by an *n*-rank tensor which is characterized in principle by 3^n components.

The real number of independent components is normally $< 3^n$ **for two reasons**:

(1) Inherent characteristics of the property

(2) Constrains put either by the crystal or the site symmetry.