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*Volume D*  
PHYSICAL PROPERTIES OF CRYSTALS

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*Edited by*  
A. AUTHIER

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## Preface to the second edition

BY ANDRÉ AUTHIER

The first edition of Volume D appeared in 2003. This second edition includes a new chapter and eight chapters have been updated, three of them extensively, with entirely new sections included.

Volume D deals with the influence of symmetry on the physical and tensor properties of crystals and on their structural phase transitions. It is an up-to-date account of the physical properties of crystals, with many useful tables, aimed at a wide readership in the fields of mineralogy, crystallography, solid-state physics and materials science; it brings together various topics that are usually to be found in quite different handbooks but that have in common their tensor nature and the role of crystallographic symmetry. The overall structure of the volume has remained unchanged.

Part 1 introduces the mathematical properties of tensors and group representations, and gives their independent components for each of the crystallographic groups. Several examples of tensor properties are described: elastic properties, thermal expansion, magnetic properties, linear and nonlinear optical properties, transport properties, atomic displacement parameters, and local electric susceptibility. A new section presenting multiferroics, a field which has seen big progress in recent years, has been added to Chapter 1.5 on magnetic properties. A new

chapter (Chapter 1.11) deals with the tensor properties of local crystal properties. It considers the impact of symmetry on local physical properties. The symmetry and physical phenomena that allow and restrict forbidden reflections excited at radiation energies close to X-ray absorption edges of atoms are described; reflections caused by magnetic scattering are also discussed.

Part 2 is devoted to the symmetry aspects of excitations in reciprocal space: phonons, electrons, Raman scattering and Brillouin scattering.

Part 3 deals with the symmetry aspects of structural phase transitions and twinning. Chapter 3.3, *Twinning of crystals*, has been considerably updated with a large new section on the effect of twinning in reciprocal space, and a section on the relations between twinning and domain structure, the topic of Chapter 3.4, which has also been entirely updated, with new tables and new figures.

It is a pleasure to thank all the authors who have updated their contributions and the authors of the new chapter. I am particularly grateful to the Technical Editor, Nicola Ashcroft, who incorporated all the corrections, sometimes quite complicated, to the existing chapters, and who edited the new chapter and the new sections with speed, highly professional efficiency and good humour.

# 1.1. Introduction to the properties of tensors

BY A. AUTHIER

## 1.1.1. The matrix of physical properties

### 1.1.1.1. Notion of extensive and intensive quantities

Physical laws express in general the response of a medium to a certain influence. Most physical properties may therefore be defined by a relation coupling two or more measurable quantities. For instance, the specific heat characterizes the relation between a variation of temperature and a variation of entropy at a given temperature in a given medium, the dielectric susceptibility the relation between electric field and electric polarization, the elastic constants the relation between an applied stress and the resulting strain *etc.* These relations are between quantities of the same nature: thermal, electrical and mechanical, respectively. But there are also cross effects, for instance:

(a) *thermal expansion* and *piezocaloric effect*: mechanical reaction to a thermal impetus or the reverse;

(b) *pyroelectricity* and *electrocaloric effect*: electrical response to a thermal impetus or the reverse;

(c) *piezoelectricity* and *electrostriction*: electric response to a mechanical impetus;

(d) *piezomagnetism* and *magnetostriction*: magnetic response to a mechanical impetus;

(e) *photoelasticity*: birefringence produced by stress;

(f) *acousto-optic effect*: birefringence produced by an acoustic wave;

(g) *electro-optic effect*: birefringence produced by an electric field;

(h) *magneto-optic effect*: appearance of a rotatory polarization under the influence of a magnetic field.

The physical quantities that are involved in these relations can be divided into two categories:

(i) *extensive quantities*, which are proportional to the volume of matter or to the mass, that is to the number of molecules in the medium, for instance entropy, energy, quantity of electricity *etc.* One uses frequently specific extensive parameters, which are given per unit mass or per unit volume, such as the specific mass, the electric polarization (dipole moment per unit volume) *etc.*

(ii) *intensive parameters*, quantities whose product with an extensive quantity is homogeneous to an energy. For instance, volume is an extensive quantity; the energy stored by a gas undergoing a change of volume  $dV$  under pressure  $p$  is  $p dV$ . Pressure is therefore the intensive parameter associated with volume. Table 1.1.1.1 gives examples of extensive quantities and of the related intensive parameters.

### 1.1.1.2. Notion of tensor in physics

Each of the quantities mentioned in the preceding section is represented by a mathematical expression. Some are direction independent and are represented by *scalars*: specific mass, specific heat, volume, pressure, entropy, temperature, quantity of electricity, electric potential. Others are direction dependent and are represented by *vectors*: force, electric field, electric displacement, the gradient of a scalar quantity. Still others cannot be represented by scalars or vectors and are represented by more complicated mathematical expressions. Magnetic quantities are represented by *axial vectors* (or *pseudovectors*), which are a particular kind of tensor (see Section 1.1.4.5.3). A few examples will show the necessity of using tensors in physics and Section 1.1.3 will present elementary mathematical properties of tensors.

(i) *Thermal expansion*. In an isotropic medium, thermal expansion is represented by a single number, a scalar, but this is

not the case in an anisotropic medium: a sphere cut in an anisotropic medium becomes an ellipsoid when the temperature is varied and thermal expansion can no longer be represented by a single number. It is actually represented by a tensor of rank 2.

(ii) *Dielectric constant*. In an isotropic medium of a perfect dielectric we can write, in SI units,

$$\begin{aligned}\mathbf{P} &= \varepsilon_0 \chi_e \mathbf{E} \\ \mathbf{D} &= \varepsilon_0 \mathbf{E} + \mathbf{P} = \varepsilon_0(1 + \chi_e) \mathbf{E} = \varepsilon \mathbf{E},\end{aligned}$$

where  $\mathbf{P}$  is the electric polarization (= dipole moment per unit volume),  $\varepsilon_0$  the permittivity of vacuum,  $\chi_e$  the dielectric susceptibility,  $\mathbf{D}$  the electric displacement and  $\varepsilon$  the dielectric constant, also called dielectric permittivity. These expressions indicate that the electric field, on the one hand, and polarization and displacement, on the other hand, are linearly related. In the general case of an anisotropic medium, this is no longer true and one must write expressions indicating that the components of the displacement are linearly related to the components of the field:

$$\begin{cases} D^1 = \varepsilon_1^1 E^1 + \varepsilon_1^2 E^2 + \varepsilon_1^3 E^3 \\ D^2 = \varepsilon_2^1 E^1 + \varepsilon_2^2 E^2 + \varepsilon_2^3 E^3 \\ D^3 = \varepsilon_3^1 E^1 + \varepsilon_3^2 E^2 + \varepsilon_3^3 E^3. \end{cases} \quad (1.1.1.1)$$

The dielectric constant is now characterized by a set of nine components  $\varepsilon_i^j$ ; they are the components of a tensor of rank 2. It will be seen in Section 1.1.4.5.2.1 that this tensor is symmetric ( $\varepsilon_i^j = \varepsilon_j^i$ ) and that the number of independent components is equal to six.

(iii) *Stressed rod (Hooke's law)*. If one pulls a rod of length  $\ell$  and cross section  $\mathcal{A}$  with a force  $F$ , its length is increased by a quantity  $\Delta\ell$  given by  $\Delta\ell/\ell = (1/E)F/\mathcal{A}$ , where  $E$  is Young's modulus, or elastic stiffness (see Section 1.3.3.1). But, at the same time, the radius,  $r$ , decreases by  $\Delta r$  given by  $\Delta r/r = -(v/E)F/\mathcal{A}$ , where  $v$  is Poisson's ratio (Section 1.3.3.4.3). It can be seen that a scalar is not sufficient to describe the elastic deformation of a material, even if it is isotropic. The number of independent components depends on the symmetry of the medium and it will be seen that they are the components of a tensor of rank 4. It was precisely to describe the properties of elasticity by a mathematical expression that the notion of a tensor was introduced in physics by W. Voigt in the 19th century (Voigt, 1910) and by L. Brillouin in the first half of the 20th century (Brillouin, 1949).

Table 1.1.1.1. *Extensive quantities and associated intensive parameters*

The last four lines of the table refer to properties that are time dependent.

Extensive quantities	Intensive parameters
Volume	Pressure
Strain	Stress
Displacement	Force
Entropy	Temperature
Quantity of electricity	Electric potential
Electric polarization	Electric field
Electric displacement	Electric field
Magnetization	Magnetic field
Magnetic induction	Magnetic field
Reaction rate	Chemical potential
Heat flow	Temperature gradient
Diffusion of matter	Concentration gradient
Electric current	Potential gradient



## 1.1. INTRODUCTION TO THE PROPERTIES OF TENSORS

### 1.1.4.1. Introduction – Neumann’s principle

We saw in Section 1.1.1 that physical properties express in general the response of a medium to an impetus. It has been known for a long time that symmetry considerations play an important role in the study of physical phenomena. These considerations are often very fruitful and have led, for instance, to the discovery of piezoelectricity by the Curie brothers in 1880 (Curie & Curie, 1880, 1881). It is not unusual for physical properties to be related to asymmetries. This is the case in electrical polarization, optical activity *etc.* The first to codify this role was the German physicist and crystallographer F. E. Neumann (1795–1898). In a series of papers (Neumann, 1832, 1833, 1834) he had studied the relations between the orientations of the mechanical, thermal and optical axes on the one hand and that of the crystalline axes on the other. His principle of symmetry was first stated in his course at the University of Königsberg (1873/1874) and was published in the printed version of his lecture notes (Neumann, 1885). It is now called *Neumann’s principle*: *if a crystal is invariant with respect to certain symmetry elements, any of its physical properties must also be invariant with respect to the same symmetry elements.*

This principle may be illustrated by considering the optical properties of a crystal. In an anisotropic medium, the index of refraction depends on direction. For a given wave normal, two waves may propagate, with different velocities; this is the double refraction effect. The indices of refraction of the two waves vary with direction and can be found by using the index ellipsoid known as the *optical indicatrix* (see Section 1.6.3.2). Consider the central section of the ellipsoid perpendicular to the direction of propagation of the wave. It is an ellipse. The indices of the two waves that may propagate along this direction are equal to the semi-axes of that ellipse. There are two directions for which the central section is circular, and therefore two wave directions for which there is no double refraction. These directions are called optic axes, and the medium is said to be *biaxial*. If the medium is invariant with respect to a threefold, a fourfold or a sixfold axis (as in a trigonal, tetragonal or hexagonal crystal, for instance), its ellipsoid must also be invariant with respect to the same axis, according to Neumann’s principle. As an ellipsoid can only be ordinary or of revolution, the indicatrix of a trigonal, tetragonal or hexagonal crystal is necessarily an ellipsoid of revolution that has only one circular central section and one optic axis. These crystals are said to be *uniaxial*. In a cubic crystal that has four threefold axes, the indicatrix must have several axes of revolution, it is therefore a sphere, and cubic media behave as isotropic media for properties represented by a tensor of rank 2.

### 1.1.4.2. Curie laws

The example given above shows that the symmetry of the property may possess a higher symmetry than the medium. The property is represented in that case by the indicatrix. The symmetry of an ellipsoid is

$$\frac{A_2}{M} \frac{A_2'}{M'} \frac{A_2''}{M''} C = mmm \text{ for any ellipsoid}$$

(orthorhombic symmetry)

$$\frac{A_\infty}{M} \frac{\infty A_2}{\infty M} C = \frac{\infty}{m} m \text{ for an ellipsoid of revolution}$$

(cylindrical symmetry)

$$\infty \frac{A_\infty}{M} C = \infty \frac{\infty}{m} \text{ for a sphere}$$

(spherical symmetry).

[Axes  $A_\infty$  are axes of revolution, or *axes of isotropy*, introduced by Curie (1884, 1894), *cf. International Tables for Crystallography* (2005), Vol. A, Table 10.1.4.2.]

The symmetry of the indicatrix is identical to that of the medium if the crystal belongs to the orthorhombic holohedry and is higher in all other cases.

This remark is the basis of the generalization of the symmetry principle by P. Curie (1859–1906). He stated that (Curie, 1894):

(i) *the symmetry characteristic of a phenomenon is the highest compatible with the existence of the phenomenon;*

(ii) *the phenomenon may exist in a medium that possesses that symmetry or that of a subgroup of that symmetry;*

and concludes that some symmetry elements may coexist with the phenomenon but that their presence is not necessary. On the contrary, what is necessary is the *absence* of certain symmetry elements: ‘asymmetry creates the phenomenon’ (*‘C’est la dissymétrie qui crée le phénomène’*; Curie, 1894, p. 400). Noting that physical phenomena usually express relations between a cause and an effect (an influence and a response), P. Curie restated the two above propositions in the following way, now known as Curie laws, although they are not, properly speaking, laws:

(i) *the asymmetry of the effects must pre-exist in the causes;*

(ii) *the effects may be more symmetric than the causes.*

The application of the Curie laws enable one to determine the symmetry characteristic of a phenomenon. Let us consider the phenomenon first as an effect. If  $\Phi$  is the symmetry of the phenomenon and  $C$  the symmetry of the cause that produces it,

$$C \leq \Phi.$$

Let us now consider the phenomenon as a cause producing a certain effect with symmetry  $E$ :

$$\Phi \leq E.$$

We can therefore conclude that

$$C \leq \Phi \leq E.$$

If we choose among the various possible causes the most symmetric one, and among the various possible effects the one with the lowest symmetry, we can then determine the symmetry that characterizes the phenomenon.

As an example, let us determine the symmetry associated with a mechanical force. A force can be considered as the result of a traction effort, the symmetry of which is  $A_\infty \infty M$ . If considered as a cause, its effect may be the motion of a sphere in a given direction (for example, a spherical ball falling under its own weight). Again, the symmetry is  $A_\infty \infty M$ . The symmetries associated with the force considered as a cause and as an effect being the same, we may conclude that  $A_\infty \infty M$  is its characteristic symmetry.

### 1.1.4.3. Symmetries associated with an electric field and with magnetic induction (flux density)

#### 1.1.4.3.1. Symmetry of an electric field

Considered as an effect, an electric field may have been produced by two circular coaxial electrodes, the first one carrying positive electric charges, the other one negative charges (Fig. 1.1.4.1). The cause possesses an axis of revolution and an infinity

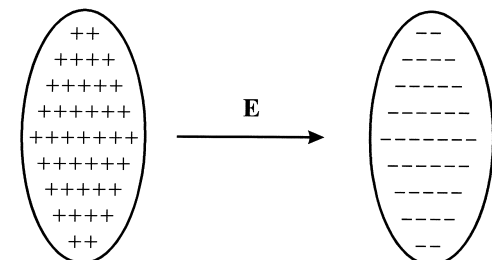


Fig. 1.1.4.1. Symmetry of an electric field.

## 1.2. Representations of crystallographic groups

BY T. JANSSEN

### 1.2.1. Introduction

Symmetry arguments play an important role in science. Often one can use them in a heuristic way, but the correct formulation is in terms of group theory. This remark is in fact superfluous for crystallographers, who are used to point groups and space groups as they occur in the description of structures. However, besides these structural problems there are many others where group theory may play a role. A central role in this context is played by representation theory, which treats the action of a group on physical quantities, and usually this is done in terms of linear transformations, although nonlinear representations may also occur.

To start with an example, consider a spin system, an arrangement of spins on sites with a certain symmetry, for example space-group symmetry. The elements of the space group map the sites onto other sites, but at the same time the spins are rotated or transformed otherwise in a well defined fashion. The spins can be seen as elements of a vector space (spin space) and the transformation in this space is an image of the space-group element. In a similar way, all symmetric tensors of rank 2 form a vector space, because one can add them and multiply them by a real factor. A linear change of coordinates changes the vectors, and the transformations in the space of tensors are the image of the coordinate transformations. Probably the most important use of such representations is in quantum mechanics, where transformations in coordinate space are mapped onto linear transformations in the quantum mechanical space of state vectors.

To see the relation between groups of transformations and the use of their representations in physics, consider a tensor which transforms under a certain point group. Let us take a symmetric rank 2 tensor  $T_{ij}$  in three dimensions. We take as example the point group 222. From Section 1.1.3.2 one knows how such a tensor transforms: it transforms into a tensor  $T'_{ij}$  according to

$$T'_{ij} = \sum_{k=1}^3 \sum_{m=1}^3 R_{ik} R_{jm} T_{km} \quad (1.2.1.1)$$

for all orthogonal transformations  $R$  in the group 222. This action of the point group 222 is obviously a linear one:

$$(c_1 T_{ij}^{(1)} + c_2 T_{ij}^{(2)})' = c_1 T_{ij}^{(1)'} + c_2 T_{ij}^{(2)'}$$

The transformations on the tensors really form an image of the group, because if one writes  $D(R)T$  for  $T'$ , one has for two elements  $R^{(1)}$  and  $R^{(2)}$  the relation

$$(D(R^{(1)}R^{(2)}))T = D(R^{(1)})(D(R^{(2)})T)$$

or

$$D(R^{(1)}R^{(2)}) = D(R^{(1)})D(R^{(2)}). \quad (1.2.1.2)$$

This property is said to define a (linear) representation. Because of the representation property, it is sufficient to know how the tensor transforms under the generators of a group. In our example, one could be interested in symmetric tensors that are invariant under the group 222. Then it is sufficient to consider the rotations over  $180^\circ$  along the  $x$  and  $y$  axes. If the point group is a symmetry group of the system, a tensor describing the relation between two physical quantities should remain the same. For invariant tensors one has

$$\begin{aligned} & \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{12} & a_{22} & a_{23} \\ a_{13} & a_{23} & a_{33} \end{pmatrix} \\ &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{12} & a_{22} & a_{23} \\ a_{13} & a_{23} & a_{33} \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \\ & \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{12} & a_{22} & a_{23} \\ a_{13} & a_{23} & a_{33} \end{pmatrix} \\ &= \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{12} & a_{22} & a_{23} \\ a_{13} & a_{23} & a_{33} \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \end{aligned}$$

and the solution of these equations is

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{12} & a_{22} & a_{23} \\ a_{13} & a_{23} & a_{33} \end{pmatrix} = \begin{pmatrix} a_{11} & 0 & 0 \\ 0 & a_{22} & 0 \\ 0 & 0 & a_{33} \end{pmatrix}.$$

The matrices of rank 2 form a nine-dimensional vector space. The rotation over  $180^\circ$  around the  $x$  axis can also be written as

$$R \begin{pmatrix} a_{11} \\ a_{12} \\ a_{13} \\ a_{21} \\ a_{22} \\ a_{23} \\ a_{31} \\ a_{32} \\ a_{33} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} a_{11} \\ a_{12} \\ a_{13} \\ a_{21} \\ a_{22} \\ a_{23} \\ a_{31} \\ a_{32} \\ a_{33} \end{pmatrix}.$$

This nine-dimensional matrix together with the one corresponding to a rotation along the  $y$  axis generate a representation of the group 222 in the nine-dimensional space of three-dimensional rank 2 tensors. The invariant tensors form the subspace  $(a_{11}, 0, 0, 0, a_{22}, 0, 0, 0, a_{33})$ . In this simple case, group theory is barely needed. However, in more complex situations, the calculations may become quite cumbersome without group theory. Moreover, group theory may give a wealth of other information, such as selection rules and orthogonality relations, that can be obtained only with much effort without group theory, or in particular representation theory. Tables of tensor properties, and irreducible representations of point and space groups, have been in use for a long time. For point groups see, for example, Butler (1981) and Altmann & Herzig (1994); for space groups, see Miller & Love (1967), Kovalev (1987) and Stokes & Hatch (1988).

In the following, we shall discuss the representation theory of crystallographic groups. We shall adopt a slightly abstract language, which has the advantage of conciseness and generality, but we shall consider examples of the most important notions. Another point that could give rise to some problems is the fact that we shall consider in part the theory for crystallographic groups in arbitrary dimension. Of course, physics occurs in three-

# 1. TENSORIAL ASPECTS OF PHYSICAL PROPERTIES

Table 1.2.6.5. Irreducible representations and character tables for the 32 crystallographic point groups in three dimensions

(a)  $C_1$

$C_1$	$\varepsilon$
$n$	1
Order	1
$\Gamma_1$	1

$$1 \quad \Gamma_1 : A = \chi_1 \quad x, y, z \quad x^2, y^2, z^2, yz, xz, xy$$

(e)  $C_6$  [ $\omega = \exp(\pi i/3)$ ].

$C_6$	$\varepsilon$	$\alpha$	$\alpha^2$	$\alpha^3$	$\alpha^4$	$\alpha^5$
$n$	1	1	1	1	1	1
Order	1	6	3	2	3	6
$\Gamma_1$	1	1	1	1	1	1
$\Gamma_2$	1	$\omega$	$\omega^2$	-1	$-\omega$	$-\omega^2$
$\Gamma_3$	1	$\omega^2$	$-\omega$	1	$\omega^2$	$-\omega$
$\Gamma_4$	1	-1	1	-1	1	-1
$\Gamma_5$	1	$-\omega$	$\omega^2$	1	$-\omega$	$\omega^2$
$\Gamma_6$	1	$-\omega^2$	$-\omega$	-1	$\omega^2$	$\omega$

(b)  $C_2$

$C_2$	$\varepsilon$	$\alpha$
$n$	1	1
Order	1	2
$\Gamma_1$	1	1
$\Gamma_2$	1	-1

$$2 \quad \alpha = C_{2z} \quad \Gamma_1 : A = \chi_1 \quad z \quad x^2, y^2, z^2, xy$$

$$C_2 \quad \Gamma_2 : B = \chi_3 \quad x, y \quad yz, xz$$
  

$$m \quad \alpha = \sigma_z \quad \Gamma_1 : A' = \chi_1 \quad x, y \quad x^2, y^2, z^2, xy$$

$$C_s \quad \Gamma_2 : A'' = \chi_3 \quad z \quad yz, xz$$
  

$$\bar{1} \quad \alpha = I \quad \Gamma_1 : A_g = \chi_1^+ \quad x^2, y^2, z^2, yz, xz, xy$$

$$C_i \quad \Gamma_2 : A_u = \chi_1^- \quad x, y, z$$

Matrices of the real representations:

	$\Gamma_2 \oplus \Gamma_6$	$\Gamma_3 \oplus \Gamma_5$
$\varepsilon$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$
$\alpha$	$\begin{pmatrix} 1 & -1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ 1 & -1 \end{pmatrix}$
$\alpha^2$	$\begin{pmatrix} 0 & -1 \\ 1 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 1 \\ -1 & 0 \end{pmatrix}$
$\alpha^3$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$
$\alpha^4$	$\begin{pmatrix} -1 & 1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ 1 & -1 \end{pmatrix}$
$\alpha^5$	$\begin{pmatrix} 0 & 1 \\ -1 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 1 \\ -1 & 0 \end{pmatrix}$

(c)  $C_3$  [ $\omega = \exp(2\pi i/3)$ ].

$C_3$	$\varepsilon$	$\alpha$	$\alpha^2$
$n$	1	1	1
Order	1	3	3
$\Gamma_1$	1	1	1
$\Gamma_2$	1	$\omega$	$\omega^2$
$\Gamma_3$	1	$\omega^2$	$\omega$

Matrices of the real two-dimensional representation:

	$\varepsilon$	$\alpha$	$\alpha^2$
$\Gamma_2 \oplus \Gamma_3$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ 1 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 1 \\ -1 & 0 \end{pmatrix}$

$$3 \quad \alpha = C_{3z} \quad \Gamma_1 : A = \chi_1 \quad z \quad x^2 + y^2, z^2$$

$$C_3 \quad \Gamma_2 \oplus \Gamma_3 : E = \chi_{1c} + \chi_{1c}^* \quad x, y \quad x^2 - y^2, xz, yz, xy$$

$$6 \quad \alpha = C_{6z} \quad \Gamma_1 : A = \chi_1 \quad z \quad x^2 + y^2, z^2$$

$$C_6 \quad \Gamma_4 : B = \chi_3 \quad x, y \quad xz, yz$$

$$\Gamma_2 \oplus \Gamma_6 : E_1 = \chi_{1c} + \chi_{1c}^* \quad x, y \quad x^2 - y^2, xy$$

$$\Gamma_3 \oplus \Gamma_5 : E_2 = \chi_{2c} + \chi_{2c}^* \quad x, y \quad x^2 - y^2, xy$$

$$\bar{3} \quad \alpha = S_{3z} \quad \Gamma_1 : A_g = \chi_1^+ \quad x^2 + y^2, z^2$$

$$S_6 \quad \Gamma_4 : A_u = \chi_1^- \quad z$$

$$\Gamma_2 \oplus \Gamma_6 : E_u = \chi_{1c}^- + \chi_{1c}^{*-} \quad x, y$$

$$\Gamma_3 \oplus \Gamma_5 : E_g = \chi_{1c}^+ + \chi_{1c}^{*+} \quad x^2 - y^2, xy, xz, yz$$

$$\bar{6} \quad \alpha = S_{6z} \quad \Gamma_1 : A' = \chi_1 \quad x^2 + y^2, z^2$$

$$C_{3h} \quad \Gamma_4 : A'' = \chi_3 \quad z$$

$$\Gamma_2 \oplus \Gamma_6 : E' = \chi_{2c} + \chi_{2c}^* \quad xz, yz$$

$$\Gamma_3 \oplus \Gamma_5 : E'' = \chi_{1c} + \chi_{1c}^* \quad x, y \quad x^2 - y^2, xy$$

(d)  $C_4$

$C_4$	$\varepsilon$	$\alpha$	$\alpha^2$	$\alpha^3$
$n$	1	1	1	1
Order	1	4	2	4
$\Gamma_1$	1	1	1	1
$\Gamma_2$	1	$i$	-1	$-i$
$\Gamma_3$	1	-1	1	-1
$\Gamma_4$	1	$-i$	-1	$i$

Matrices of the real two-dimensional representation:

	$\varepsilon$	$\alpha$	$\alpha^2$	$\alpha^3$
$\Gamma_2 \oplus \Gamma_4$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$

$$4 \quad \alpha = C_{4z} \quad \Gamma_1 : A = \chi_1 \quad z \quad x^2 + y^2, z^2$$

$$C_4 \quad \Gamma_3 : B = \chi_3 \quad x^2 - y^2, xy$$

$$\Gamma_2 \oplus \Gamma_4 : E = \chi_{1c} + \chi_{1c}^* \quad x, y \quad yz, xz$$
  

$$\bar{4} \quad \alpha = S_4 \quad \Gamma_1 : A = \chi_1 \quad x^2 + y^2, z^2$$

$$S_4 \quad \Gamma_3 : B = \chi_3 \quad z \quad x^2 - y^2, xy$$

$$\Gamma_2 \oplus \Gamma_4 : E = \chi_{1c} + \chi_{1c}^* \quad x, y \quad yz, xz$$

(f)  $D_2$

$D_2$	$\varepsilon$	$\alpha$	$\beta$	$\alpha\beta$
$n$	1	1	1	1
Order	1	2	2	2
$\Gamma_1$	1	1	1	1
$\Gamma_2$	1	1	-1	-1
$\Gamma_3$	1	-1	1	-1
$\Gamma_4$	1	-1	-1	1

$$222 \quad \alpha = C_{2x} \quad \Gamma_1 : A_1 = \chi_1 \quad x^2, y^2, z^2$$

$$D_2 \quad \beta = C_{2y} \quad \Gamma_2 : B_3 = \chi_3 \quad x \quad yz$$

$$\alpha\beta = C_{2z} \quad \Gamma_3 : B_2 = \chi_4 \quad y \quad xz$$

$$\Gamma_4 : B_1 = \chi_2 \quad z \quad xz$$

$$mm2 \quad \alpha = C_{2z} \quad \Gamma_1 : A_1 = \chi_1 \quad z \quad x^2, y^2, z^2$$

$$C_{2v} \quad \beta = \sigma_x \quad \Gamma_2 : A_2 = \chi_2 \quad xy$$

$$\alpha\beta = \sigma_y \quad \Gamma_3 : B_2 = \chi_3 \quad y \quad yz$$

$$\Gamma_4 : B_1 = \chi_4 \quad x \quad xz$$

$$2/m \quad \alpha = C_{2z} \quad \Gamma_1 : A_g = \chi_1^+ \quad x^2, y^2, z^2, xy$$

$$C_{2h} \quad \beta = \sigma_z \quad \Gamma_2 : A_u = \chi_1^- \quad z \quad z$$

$$\alpha\beta = I \quad \Gamma_3 : B_u = \chi_3^- \quad x, y$$

$$\Gamma_4 : B_g = \chi_3^+ \quad x, y$$

### 1.3. ELASTIC PROPERTIES

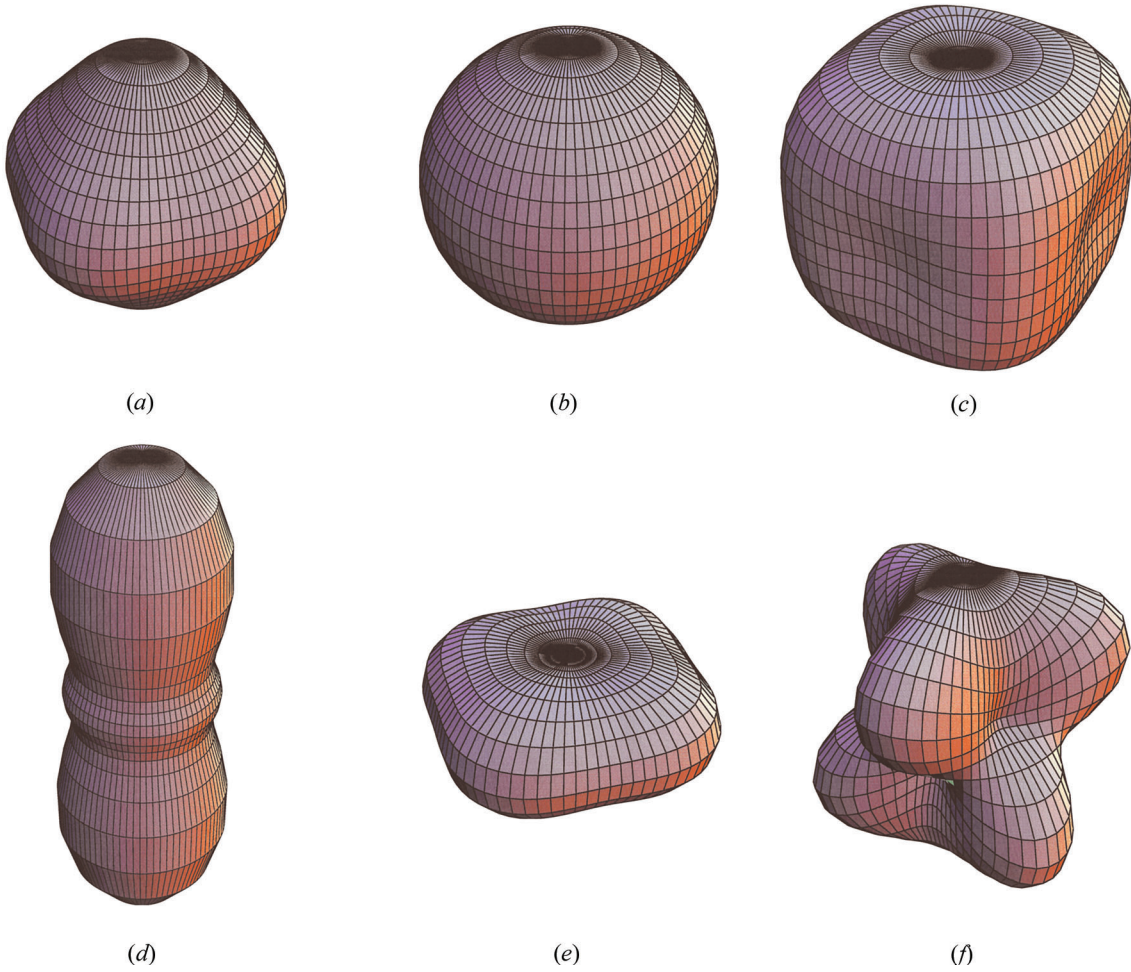


Fig. 1.3.3.4. Representation surface of the inverse of Young's modulus. (a) Al, cubic, anisotropy factor  $> 1$ ; (b) W, cubic, anisotropy factor  $= 1$ ; (c) NaCl, cubic, anisotropy factor  $< 1$ ; (d) Zn, hexagonal; (e) Sn, tetragonal; (f) calcite, trigonal.

$$\begin{aligned}
 T_1 &= c_{11}S_1 + c_{12}(S_2 + S_3) & T_1 &= 2\mu S_1 + \lambda(S_1 + S_2 + S_3) \\
 T_2 &= c_{12}S_1 + c_{11}S_2 + c_{12}S_3 & T_2 &= 2\mu S_2 + \lambda(S_1 + S_2 + S_3) \\
 T_3 &= c_{12}(S_1 + S_2) + c_{11}S_3 & T_3 &= 2\mu S_3 + \lambda(S_1 + S_2 + S_3).
 \end{aligned} \tag{1.3.3.16}$$

These relations can equally well be written in the symmetrical form

$$\begin{aligned}
 T_1 &= (c_{11} - c_{12})S_1 + c_{12}(S_1 + S_2 + S_3) \\
 T_2 &= (c_{11} - c_{12})S_2 + c_{12}(S_1 + S_2 + S_3) \\
 T_3 &= (c_{11} - c_{12})S_3 + c_{12}(S_1 + S_2 + S_3).
 \end{aligned}$$

If one introduces the Lamé constants,

$$\begin{aligned}
 \mu &= (1/2)(c_{11} - c_{12}) = c_{44} \\
 \lambda &= c_{12},
 \end{aligned}$$

the equations may be written in the form often used in mechanics:

Two coefficients suffice to define the elastic properties of an isotropic material,  $s_{11}$  and  $s_{12}$ ,  $c_{11}$  and  $c_{12}$ ,  $\mu$  and  $\lambda$ ,  $\mu$  and  $\nu$ , etc. Table 1.3.3.3 gives the relations between the more common elastic coefficients.

#### 1.3.3.6. Equilibrium conditions of elasticity for isotropic media

We saw in Section 1.3.2.3 that the condition of equilibrium is

$$\partial T_{ij} / \partial x_i + \rho F_j = 0.$$

If we use the relations of elasticity, equation (1.3.3.2), this condition can be rewritten as a condition on the components of the strain tensor:

$$c_{ijkl} \frac{\partial S_{kl}}{\partial x_j} + \rho F_i = 0.$$

Table 1.3.3.3. Relations between elastic coefficients in isotropic media

Coefficient	In terms of $\mu$ and $\lambda$	In terms of $\mu$ and $\nu$	In terms of $c_{11}$ and $c_{12}$
$c_{11}$	$2\mu + \lambda$	$2\mu(1 - \nu)(1 - 2\nu)$	$c_{11}$
$c_{12}$	$\lambda$	$2\mu\nu(1 - 2\nu)$	$c_{12}$
$c_{44} = 1/s_{44}$	$\mu$	$\mu$	$(c_{11} - c_{12})/2$
$E = 1/s_{11}$	$\mu(2\mu + 3\lambda)/(\mu + \lambda)$	$2\mu(1 + \nu)$	See Section 1.3.3.2.3
$s_{12}$	$-\lambda/[2\mu(2\mu + 3\lambda)]$	$-\nu/[2\mu(1 + \nu)]$	See Section 1.3.3.2.3
$\kappa$	$3/(2\mu + 3\lambda)$	$3(1 - 2\nu)/[2\mu(1 + \nu)]$	$3/(c_{11} + 2c_{12})$
$\nu = -s_{12}/s_{11}$	$\lambda/[2(2\mu + 3\lambda)]$	$\nu$	$c_{11}/(c_{11} + c_{12})$

Recalling that

$$S_{kl} = \frac{1}{2} \left[ \frac{\partial u_k}{\partial x_l} + \frac{\partial u_l}{\partial x_k} \right],$$

the condition becomes a condition on the displacement vector,  $\mathbf{u}(\mathbf{r})$ :

### 1.3. ELASTIC PROPERTIES

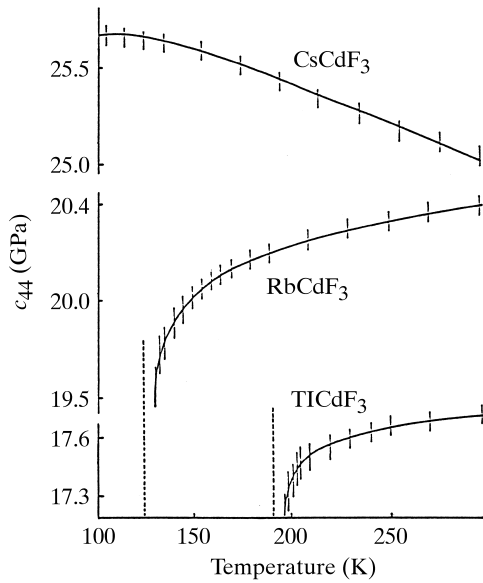


Fig. 1.3.5.3. Temperature dependence of the elastic constant  $c_{44}$  in  $\text{RbCdF}_3$ ,  $\text{CsCdF}_3$  and  $\text{TiCdF}_3$  crystals; the crystals of  $\text{RbCdF}_3$  and  $\text{TiCdF}_3$  undergo structural phase transitions (after Rousseau *et al.*, 1975).

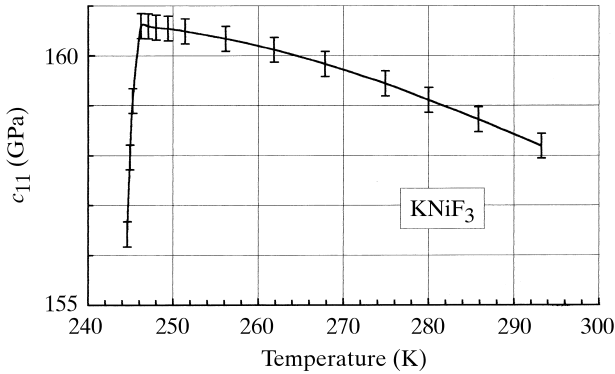


Fig. 1.3.5.4. Temperature dependence of the elastic constant  $c_{11}$  in  $\text{KNiF}_3$ , which undergoes a para-antiferromagnetic phase transition. Reprinted with permission from *Appl. Phys. Lett.* (Nouet *et al.*, 1972). Copyright (1972) American Institute of Physics.

temperature when this constant is the order parameter or is strongly coupled to the order parameter of the transformation; for instance, in the cooperative Jahn–Teller phase transition in  $\text{DyVO}_4$ ,  $(c_{11} - c_{12})/2$  is the soft acoustic phonon mode leading to the phase transition and this parameter anticipates the phase transition 300 K before it occurs (Fig. 1.3.5.5).

#### 1.3.5.3. Pressure dependence of the elastic constants

As mentioned above, anharmonic potentials are needed to explain the stress dependence of the elastic constants of a crystal. Thus, if the strain-energy density is developed in a polynomial in terms of the strain, only the first and the second elastic constants are used in linear elasticity (harmonic potentials), whereas higher-order elastic constants are also needed for nonlinear elasticity (anharmonic potentials).

Concerning the pressure dependence of the elastic constants (nonlinear elastic effect), considerable attention has been paid to

Table 1.3.5.2. Order of magnitude of the temperature dependence of the elastic stiffnesses for different types of crystals

Type of crystal	$(\partial \ln c_{11} / \partial \Theta)_p$ ( $\text{K}^{-1}$ )	$(\partial \ln c_{44} / \partial \Theta)_p$ ( $\text{K}^{-1}$ )
Ionic	$-10^{-3}$	$-3 \times 10^{-4}$
Covalent	$-10^{-4}$	$-8 \times 10^{-5}$
Metallic	$-2 \times 10^{-4}$	$-3 \times 10^{-4}$

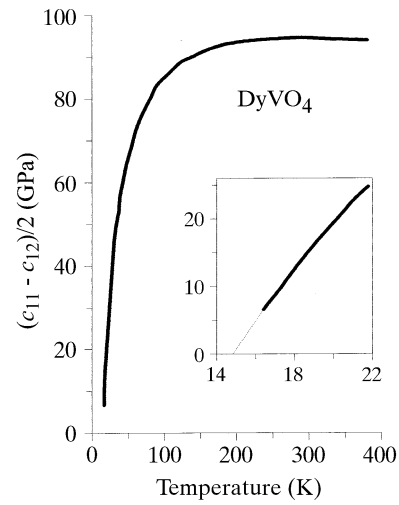


Fig. 1.3.5.5. Temperature dependence of  $(c_{11} - c_{12})/2$  in  $\text{DyVO}_4$ , which undergoes a cooperative Jahn–Teller phase transition (after Melcher & Scott, 1972).

their experimental determination since they are a unique source of significant information in many fields:

(i) In *geophysics*, a large part of the knowledge we have on the interior of the earth comes from the measurement of the transit time of elastic bursts propagating in the mantle and in the core (in the upper mantle, the average pressure is estimated to be about a few hundred GPa, a value which is comparable to that of the elastic stiffnesses of many materials).

(ii) In *solid-state physics*, the pressure dependence of the elastic constants gives significant indications concerning the stability of crystals. For example, Fig. 1.3.5.2 shows the pressure dependence of the elastic constants of  $\text{KZnF}_3$ , a cubic crystal belonging to the perovskite family. As mentioned previously, this crystal is known to be stable over a wide range of temperature and the elastic stiffnesses  $c_{ij}$  depend linearly on pressure. It may be noted that, consequently, the third-order elastic constants (TOECs) are constant. On the contrary, we observe in Fig. 1.3.5.6 that the pressure dependence of the elastic constants of  $\text{TiCdF}_3$ , a cubic crystal belonging to the same family but which is known to become unstable when the temperature is decreased to 191 K (Fischer, 1982), is nonlinear even at low pressures. In this case, the development of the strain-energy density in terms of strains elastic constant be stopped after the terms containing the third-order elastic constants; the contributions of the fourth- and fifth-order elastic constants are not negligible.

(iii) For practical use in the case of technical materials such as concrete or worked metals, the pressure dependence of the elastic moduli is also required for examining the effect of applied stresses or of an applied hydrostatic pressure, and for studying residual stresses resulting from loading (heating) and unloading (cooling) the materials.

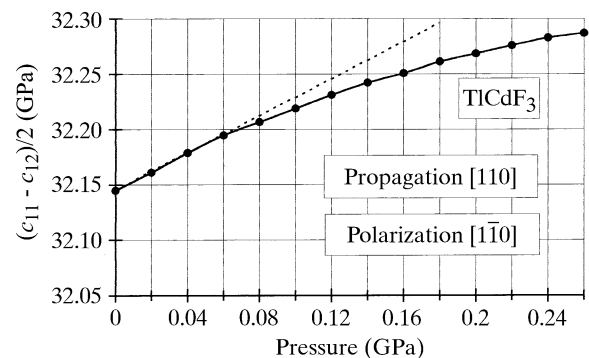


Fig. 1.3.5.6. Pressure dependence of the elastic constants  $(c_{11} - c_{12})/2$  in  $\text{TiCdF}_3$ . Reproduced with permission from *Ultrasonics Symposium Proc. IEEE* (Fischer *et al.*, 1980). Copyright (1980) IEEE.

## 1.4. THERMAL EXPANSION

It should be mentioned that the true situation is more complicated. The grain boundaries of anisotropic polycrystalline solids are subject to considerable stresses because the neighbouring grains have different amounts of expansion or contraction. These stresses may cause local plastic deformation and cracks may open up between or within the grains. These phenomena can lead to a hysteresis behaviour when the sample is heated up or cooled down. Of course, in polycrystals of a cubic crystal species, these problems do not occur.

If the polycrystalline sample exhibits a texture, the orientation distribution function (ODF) has to be considered in the averaging process. The resulting overall symmetry of a textured polycrystal is usually  $\frac{\infty}{m}m$  (see Section 1.1.4.7.4.2), showing the same tensor form as hexagonal crystals (Table 1.4.1.1), or  $mmm$ .

### 1.4.2. Grüneisen relation

Thermal expansion of a solid is a consequence of the anharmonicity of interatomic forces (see also Section 2.1.2.8). If the potentials were harmonic, the atoms would oscillate (even with large amplitudes) symmetrically about their equilibrium positions and their mean central position would remain unchanged. In order to describe thermal expansion, the anharmonicity is most conveniently accounted for by means of the so-called ‘quasiharmonic approximation’, assuming the lattice vibration frequencies  $\omega$  to be independent of temperature but dependent on volume  $[(\partial\omega/\partial V) \neq 0]$ . Anharmonicity is taken into account by letting the crystal expand, but it is assumed that the atoms vibrate about their new equilibrium positions harmonically, *i.e.* lattice dynamics are still treated in the harmonic approximation. The assumption  $(\partial\omega/\partial V) = 0$ , which is made for the harmonic oscillator, is a generalization of the postulate that the frequency of a harmonic oscillator does not depend on the amplitude of vibration.

This approach leads, as demonstrated below, to the Grüneisen relation, which combines thermal expansion with other material constants and, additionally, gives an approximate description of the temperature dependence of thermal expansion (*cf.* Krishnan *et al.*, 1979; Barron, 1998).

For isotropic media, the volume expansion  $\beta$  [ $= 3\alpha = \alpha_{11} + \alpha_{22} + \alpha_{33}$ ], *cf.* (1.4.1.2), can be expressed by the thermodynamic relation

$$\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T \left( \frac{\partial p}{\partial T} \right)_V = \kappa \left( \frac{\partial p}{\partial T} \right)_V, \quad (1.4.2.1)$$

$\kappa$  being the isothermal compressibility. To obtain the quantity  $(\partial p/\partial T)_V$ , the pressure  $p$  is deduced from the free energy  $F$ , whose differential is  $dF = -S dT - p dV$ , *i.e.* from

$$p = -(\partial F/\partial V)_T. \quad (1.4.2.2)$$

In a crystal consisting of  $N$  unit cells with  $p$  atoms in each unit cell, there are  $3p$  normal modes with frequencies  $\omega_s$  (denoted by an index  $s$  running from 1 to  $3p$ ) and with  $N$  allowed wavevectors

Table 1.4.1.1. Shape of the quadric and symmetry restrictions

System	Quadric		No. of independent components	Nonzero components
	Shape	Direction of principal axes		
Triclinic	General ellipsoid or hyperboloid	No restrictions	6	$\begin{pmatrix} \bullet & \bullet & \bullet \\ & \bullet & \bullet \\ & & \bullet \end{pmatrix}$
Monoclinic		One axis parallel to twofold axis ( <b>b</b> )	4	$\begin{pmatrix} \bullet & \cdot & \bullet \\ & \bullet & \cdot \\ & & \bullet \end{pmatrix}$
Orthorhombic		Parallel to crystallographic axes	3	$\begin{pmatrix} \bullet & \cdot & \cdot \\ & \bullet & \cdot \\ & & \bullet \end{pmatrix}$
Trigonal, tetragonal, hexagonal	Revolution ellipsoid or hyperboloid	$c$ axis is revolution axis	2	$\begin{pmatrix} \bullet & \cdot & \cdot \\ & \bullet & \cdot \\ & & \bullet \end{pmatrix}$
Cubic, isotropic media	Sphere	Arbitrary, not defined	1	$\begin{pmatrix} \bullet & \cdot & \cdot \\ & \bullet & \cdot \\ & & \bullet \end{pmatrix}$

$\mathbf{q}_t$  (denoted by an index  $t$  running from 1 to  $N$ ). Each normal mode  $\omega_s(\mathbf{q}_t)$  contributes to the free energy by the amount

$$f_{s,t} = \frac{\hbar}{2} \omega_s(\mathbf{q}_t) + kT \ln \left[ 1 - \exp \left( -\frac{\hbar \omega_s(\mathbf{q}_t)}{kT} \right) \right]. \quad (1.4.2.3)$$

The total free energy amounts, therefore, to

$$F = \sum_{s=1}^{3p} \sum_{t=1}^N f_{s,t} = \sum_{s=1}^{3p} \sum_{t=1}^N \left\{ \frac{\hbar}{2} \omega_s(\mathbf{q}_t) + kT \ln \left[ 1 - \exp \left( -\frac{\hbar \omega_s(\mathbf{q}_t)}{kT} \right) \right] \right\}. \quad (1.4.2.4)$$

From (1.4.2.2)

$$p = -\left( \frac{\partial F}{\partial V} \right)_T = -\sum_{s=1}^{3p} \sum_{t=1}^N \left\{ \frac{\hbar}{2} \frac{\partial \omega_s}{\partial V} + \frac{\exp(-\hbar \omega_s/kT) \hbar (\partial \omega_s/\partial V)}{1 - \exp(-\hbar \omega_s/kT)} \right\}. \quad (1.4.2.5)$$

The last term can be written as

$$\frac{\hbar (\partial \omega_s/\partial V)}{\exp(\hbar \omega_s/kT) - 1} = \hbar n(\omega_s(\mathbf{q}_t), T) \frac{\partial \omega_s}{\partial V}, \quad (1.4.2.6)$$

where  $n(\omega_s, T)$  is the Bose–Einstein distribution

## 1. TENSORIAL ASPECTS OF PHYSICAL PROPERTIES

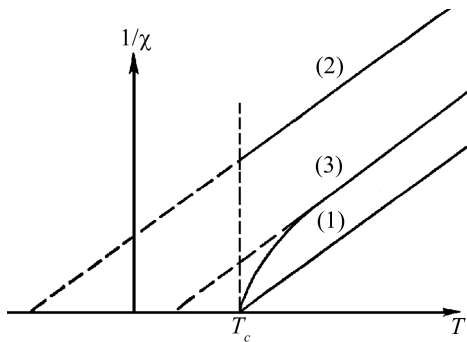


Fig. 1.5.1.1. Temperature dependence of  $1/\chi$  at high temperatures for different types of materials: (1) ferromagnet; (2) antiferromagnet; (3) ferrimagnet.

the magnetic moments (mostly exchange interaction) and to the effect of the splitting of electron levels of the paramagnetic ion in the crystalline electric field. Many paramagnets that obey the Curie–Weiss law transform into magnetically ordered materials at a temperature  $T_c$ , which is of the order of  $|\Delta|$ . The sign of  $\Delta$  depends on the sign of the exchange constant  $J^{\text{ex}}$  [see relation (1.5.1.7)]. For the substances that at low temperatures become ferromagnets, we have  $\Delta > 0$ , for antiferromagnets  $\Delta < 0$ , and for ferrimagnets the temperature dependence of  $\chi$  is more complicated (see Fig. 1.5.1.1). For those paramagnets that do not go over into an ordered state,  $\Delta$  is close to zero and equation (1.5.1.4) changes to the Curie law.

The value of the effective number of Bohr magnetons  $p$  depends strongly on the type of the magnetic ions and their environment. For most rare-earth compounds at room temperature, the number  $p$  has the same value as for free ions:

$$p = g[J(J+1)]^{1/2}, \quad (1.5.1.5)$$

where  $g$  is the Landé  $g$ -factor or the spectroscopic splitting factor ( $1 \leq g \leq 2$ ) and  $J$  is the quantum number of the total angular momentum. In this case, the paramagnetic susceptibility is practically isotropic. Some anisotropy can arise from the anisotropy of the Weiss constant  $\Delta$ .

The behaviour of the transition-metal ions is very different. In contrast to the rare-earth ions, the electrons of the partly filled shell in transition metals interact strongly with the electric field of the crystal. As a result, their energy levels are split and the orbital moments can be ‘quenched’. This means that relation (1.5.1.5) transforms to

$$p_{ij} = (g_{\text{eff}})_{ij}[S(S+1)]^{1/2}. \quad (1.5.1.6)$$

Here the value of the effective spin  $S$  represents the degeneration of the lowest electronic energy level produced by the splitting in the crystalline field;  $(g_{\text{eff}})_{ij}$  differs from the usual Landé  $g$ -factor. The values of its components lie between 0 and 10–20. The tensor  $(g_{\text{eff}})_{ij}$  becomes diagonal with respect to the principal axes. According to relation (1.5.1.6), the magnetic susceptibility also becomes a tensor. The anisotropy of  $(g_{\text{eff}})_{ij}$  can be studied using electron paramagnetic resonance (EPR) techniques.

The Curie–Weiss law describes the behaviour of those paramagnets in which the magnetization results from the competition of two forces. One is connected with the reduction of the magnetic energy by orientation of the magnetic moments of ions in the applied magnetic field; the other arises from thermal fluctuations, which resist the tendency of the field to orient these moments. At low temperatures and in strong magnetic fields, the linear dependence of the magnetization *versus* magnetic field breaks down and the magnetization can be saturated in a sufficiently strong magnetic field. Most of the paramagnetic substances that obey the Curie–Weiss law ultimately develop magnetic order as the temperature is decreased.

The conduction electrons in metals possess paramagnetism in addition to diamagnetism. The paramagnetic susceptibility of the conduction electrons is small (of the same order of magnitude as the diamagnetic susceptibility) and does not depend on temperature. This is due to the fact that the conduction electrons are governed by Fermi–Dirac statistics.

### 1.5.1.2. Magnetically ordered materials

#### 1.5.1.2.1. Ferromagnets (including ferrimagnets)

As stated above, all magnetically ordered materials that possess a spontaneous magnetization  $\mathbf{M}_s$  different from zero (a magnetization even in zero magnetic field) are called ferromagnets. The simplest type of ferromagnet is shown in Fig. 1.5.1.2(a). This type possesses only one kind of magnetic ion or atom. All their magnetic moments are aligned parallel to each other in the same direction. This magnetic structure is characterized by one vector  $\mathbf{M}$ . It turns out that there are very few ferromagnets of this type in which only atoms or ions are responsible for the ferromagnetic magnetization (CrBr<sub>3</sub>, EuO *etc.*). The overwhelming majority of ferromagnets of this simplest type are metals, in which the magnetization is the sum of the magnetic moments of the localized ions and of the conduction electrons, which are partly polarized.

More complicated is the type of ferromagnet which is called a ferrimagnet. This name is derived from the name of the oxides of the elements of the iron group. As an example, Fig. 1.5.1.2(b) schematically represents the magnetic structure of magnetite (Fe<sub>3</sub>O<sub>4</sub>). It contains two types of magnetic ions and the number of Fe<sup>3+</sup> ions ( $\mu_1$  and  $\mu_2$ ) is twice the number of Fe<sup>2+</sup> ions ( $\mu_3$ ). The values of the magnetic moments of these two types of ions differ. The magnetic moments of all Fe<sup>2+</sup> ions are aligned in one direction. The Fe<sup>3+</sup> ions are divided into two parts: the magnetic moments of one half of these ions are aligned parallel to the magnetic moments of Fe<sup>2+</sup> and the magnetic moments of the other half are aligned antiparallel. The array of all magnetic moments of identical ions oriented in one direction is called a magnetic sublattice. The magnetization vector of a given sublattice will be denoted by  $\mathbf{M}_i$ . Hence the magnetic structure of Fe<sub>3</sub>O<sub>4</sub> consists of three magnetic sublattices. The magnetizations of two of them are aligned in one direction, the magnetization of the third one is oriented in the opposite direction. The net ferromagnetic magnetization is  $M_s = M_1 - M_2 + M_3 = M_3$ .

The special feature of ferrimagnets, as well as of many antiferromagnets, is that they consist of sublattices aligned antiparallel to each other. Such a structure is governed by the nature of the main interaction responsible for the formation of the ordered magnetic structures, the exchange interaction. The energy of the exchange interaction does not depend on the direction of the interacting magnetic moments (or spins  $\mathbf{S}$ ) relative to the crystallographic axes and is represented by the following relation:

$$U_{\text{ex}} = - \sum_{m,n} J_{mn}^{\text{ex}} \mathbf{S}_m \mathbf{S}_n. \quad (1.5.1.7)$$

Here  $\mathbf{S}_m, \mathbf{S}_n$  are the spins of magnetic atoms (ions) and  $J_{mn}^{\text{ex}}$  is the exchange constant, which usually decreases fast when the distance between the atoms rises. Therefore, usually only the nearest-neighbour interaction needs to be taken into account. Hence, according to (1.5.1.7), the exchange energy is a minimum for the state in which neighbouring spins are parallel (if  $J^{\text{ex}} > 0$ ) or antiparallel (if  $J^{\text{ex}} < 0$ ). If the nearest-neighbour exchange interaction were the only interaction responsible for the magnetic ordering, only collinear magnetic structures would exist (except in triangle lattices). Together with the exchange interaction, there is also a magnetic dipole interaction between the magnetic moments of the atoms as well as an interaction of the atomic magnetic electrons with the crystalline electric field. These interactions are much smaller than the exchange interaction.

## 1.5. MAGNETIC PROPERTIES

in Table 1.5.8.3. Bloembergen (1962) pointed out that all these paramagnets are piezoelectric crystals. He called the ME effect in these substances the *paramagnetolectric* (PME) effect. It is defined by the nonzero components of the tensor  $\beta_{ijk}$ :

$$P_i = \frac{1}{2} \beta_{ijk} H_j H_k, \quad (1.5.8.11)$$

$$\mu_0^* M_i = \beta_{jik} E_j H_k. \quad (1.5.8.12)$$

The PME effect was discovered by Hou & Bloembergen (1965) in  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ , which belongs to the crystallographic point group  $D_4 = 422$ . The only nonvanishing components of the third-rank tensor are  $\beta_{xyz} = \beta_{xzy} = -\beta_{yzx} = -\beta_{yxz} = \beta$  ( $\beta_{14} = -\beta_{25} = 2\beta$  in matrix notation), so that  $\mathbf{P} = \beta(H_y H_z, -H_x H_z, 0)$  and  $\mu_0^* \mathbf{M} = \beta(-E_y H_z, E_x H_z, E_x H_y - E_y H_x)$ . Both effects were observed: the polarization  $\mathbf{P}$  by applying static ( $H_z$ ) and alternating ( $H_x$  or  $H_y$ ) magnetic fields and the magnetization  $\mathbf{M}$  by applying a static magnetic field  $H_z$  and an alternating electric field in the plane  $xy$ . As a function of temperature, the PME effect shows a peak at 3.0 K and changes sign at 1.38 K. The coefficient of the PME effect at 4.2 K is

$$\begin{aligned} \beta(4.2 \text{ K}) &= 2.2 \times 10^{-9} \text{ cgs units} \\ &= 1.16 \times 10^{-18} \text{ s A}^{-1}. \end{aligned} \quad (1.5.8.13)$$

The theory developed by Hou and Bloembergen explains the PME effect by linear variation with the applied electric field of the crystal-field-splitting parameter  $D$  of the spin Hamiltonian.

Most white and black–white magnetic point groups that do not contain the inversion ( $C_i = \bar{1}$ ), either by itself or multiplied by  $R = 1'$ , admit all three types of ME effect: the linear ( $EH$ ) and two higher-order ( $EHH$  and  $HEE$ ) effects. There are many magnetically ordered compounds in which the nonlinear ME effect has been observed. Some of them are listed by Schmid (1973); more recent references are given in Schmid (1994a).

In principle, many ME effects of higher order may exist. As an example, let us consider the *piezomagnetolectric* effect. This is a combination of piezomagnetism (or piezoelectricity) and the ME effect. The thermodynamic potential  $\Phi$  must contain invariants of the form

$$\Phi = \Phi_0 - \pi_{ijk\ell} E_i H_j T_{k\ell}. \quad (1.5.8.14)$$

The problem of the piezomagnetolectric effect was considered by Rado (1962), Lyubimov (1965) and in detail by Grimmer (1992). All 69 white and black–white magnetic point groups that possess neither  $C_i = \bar{1}$  nor  $R = 1'$  admit the piezomagnetolectric effect. (These are the groups of types 2–6, 8–12, 14 and 16 in Table 1.5.8.3.) The tensor  $\pi_{ijk\ell}$ , which describes the piezomagnetolectric effect, is a tensor of rank 4, symmetric in the last two indices and invariant under space-time inversion. This effect has not been observed so far (Rivera & Schmid, 1994). Grimmer (1992) analysed in which antiferromagnets it could be observed.

### 1.5.8.3. Multiferroics<sup>4</sup>

Initially, Schmid defined multiferroics as materials with two or three primary ferroics coexisting in the same phase, such as ferromagnetism, ferroelectricity or ferroelasticity (Schmid, 1994b). The term *primary ferroics* was defined in a thermodynamic classification, distinguishing primary, secondary and tertiary ferroics (Newnham, 1974; Newnham & Cross, 1976). For magnetolectric multiferroics, however, it has become customary to loosen this definition. Magnetolectric multiferroics are now considered materials with coexisting magnetic (ferro- or antiferromagnetic) and ferroelectric order. They can be divided into two classes: multiferroics where the origins of ferroelectricity

Table 1.5.8.4. List of the magnetic point groups of the ferromagnetolectrics

Symbol of symmetry group		Allowed direction of	
Schoenflies	Hermann–Mauguin	$\mathbf{P}$	$\mathbf{M}$
$C_1$	1	Any	Any
$C_2$	2	2	2
$C_2(C_1)$	2'	2'	⊥ 2'
$C_s = C_{1h}$	$m$	$m$	⊥ $m$
$C_s(C_1)$	$m'$	$m'$	$m'$
$C_{2v}(C_2)$	$m'm'2$	2	2
$C_{2v}(C_s)$	$m'm'2'$	2'	⊥ $m$
$C_4$	4	4	4
$C_{4v}(C_4)$	$4m'm'$	4	4
$C_3$	3	3	3
$C_{3v}(C_3)$	$3m'$	3	3
$C_6$	6	6	6
$C_{6v}(C_6)$	$6m'm'$	6	6

and magnetic order are independent, and multiferroics where ferroelectricity is induced by magnetic or orbital order.

For the case of magnetically commensurate ferromagnetic ferroelectrics, Neronova & Belov (1959) pointed out that there are ten magnetic point groups that admit the simultaneous existence of spontaneous ferroelectric polarization  $\mathbf{P}$  and magnetic polarization  $\mathbf{M}$ , which they called ferromagnetolectrics. Neronova and Belov considered only structures with parallel alignment of  $\mathbf{P}$  and  $\mathbf{M}$  (or  $\mathbf{L}$ ). There are three more groups that allow the coexistence of ferroelectric and ferromagnetic order, in which  $\mathbf{P}$  and  $\mathbf{M}$  are perpendicular to each other. Shuvalov & Belov (1962) published a list of the 13 magnetic groups that admit the coexistence of ferromagnetic and ferroelectric order. These are the groups of type 4 in Table 1.5.8.3; they are given with more details in Table 1.5.8.4.

Notice that  $\mathbf{P}$  and  $\mathbf{M}$  must be parallel in eight point groups, they may be parallel in 1 and  $m'$ , and they must be perpendicular in  $2'$ ,  $m$  and  $m'm'2'$  (see also Ascher, 1970). The magnetic point groups listed in Table 1.5.8.4 admit not only ferromagnetism (and ferrimagnetism) but the first seven also admit antiferromagnetism with weak ferromagnetism. Ferroelectric pure antiferromagnets of type III<sup>a</sup> may also exist. They must belong to one of the following eight magnetic point groups (types 2 and 3 in Table 1.5.8.3):  $C_{2v} = mm2$ ;  $C_{4v} = 4mm$ ;  $C_4(C_2) = 4'$ ;  $C_{4v}(C_{2v}) = 4'mm'$ ;  $C_{3v} = 3m$ ;  $C_{6v} = 6mm$ ;  $C_6(C_3) = 6'$ ;  $C_{6v}(C_{3v}) = 6'mm'$ . Table 1.5.8.3 shows that the linear magnetolectric effect is admitted by all ferroelectric ferromagnets and all ferroelectric antiferromagnets of type III<sup>a</sup> except  $6'$  and  $6'mm'$ .

The first experimental evidence to indicate that complex perovskites may become ferromagnetolectric was observed by the Smolenskii group (see Smolenskii *et al.*, 1958). They investigated the temperature dependence of the magnetic susceptibility of the ferroelectric perovskites  $\text{Pb}(\text{Mn}_{1/2}\text{Nb}_{1/2})\text{O}_3$  and  $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ . The temperature dependence at  $T > 77 \text{ K}$  followed the Curie–Weiss law with a very large antiferromagnetic Weiss constant. Later, Astrov *et al.* (1968) proved that these compounds undergo a transition into a weakly ferromagnetic state at Néel temperatures  $T_N = 11$  and 9 K, respectively.

The single crystals of boracites synthesized by Schmid (1965) raised wide interest as examples of ferromagnetic ferroelectrics. The boracites have the chemical formula  $M_3\text{B}_7\text{O}_{13}\text{X}$  (where  $M = \text{Cu}^{2+}, \text{Ni}^{2+}, \text{Co}^{2+}, \text{Fe}^{2+}, \text{Mn}^{2+}, \text{Cr}^{2+}$  and  $X = \text{F}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{OH}^-, \text{NO}_3^-$ ). Many of them are ferroelectrics and weak ferromagnets at low temperatures. This was first shown for  $\text{Ni}_3\text{B}_7\text{O}_{13}\text{I}$  (see Ascher *et al.*, 1966). The symmetries of all the boracites are cubic at high temperatures and their magnetic point group is  $43m1'$ . As the temperature is lowered, most become ferroelectrics with the magnetic point group  $mm21'$ . At still lower temperatures, the spins of the magnetic ions in the boracites go into an antiferromagnetic state with weak ferromagnetism. For some of the boracites the ferromagnetic/ferroelectric phase belongs to the group  $m'm'2'$ , and for others to  $m'm'2$ ,  $m'$ ,  $m$  or 1. In accordance with Table 1.5.8.4, the spontaneous polarization  $\mathbf{P}$  is oriented

<sup>4</sup> Updated by M. Kenzelmann.



## 1.6. Classical linear crystal optics

BY A. M. GLAZER AND K. G. COX†

### 1.6.1. Introduction

The field of classical crystal optics is an old one, and in the last century, in particular, it was the main subject of interest in the study of crystallography. Since the advent of X-ray diffraction, however, crystal optics tended to fall out of widespread use, except perhaps in mineralogy, where it has persisted as an important technique for the classification and identification of mineral specimens. In more recent times, however, with the growth in optical communications technologies, there has been a revival of interest in the optical properties of crystals, both linear and nonlinear. There are many good books dealing with classical crystal optics, which the reader is urged to consult (Hartshorne & Stuart, 1970; Wahlstrom, 1959; Bloss, 1961). In addition, large collections of optical data on crystals exist (Groth, 1906–1919; Winchell, 1931, 1939, 1951, 1954, 1965; Kerr, 1959). In this chapter, both linear and nonlinear optical effects will be introduced briefly in a generalized way. Then the classical derivation of the refractive index surface for a crystal will be derived. This leads on to a discussion on the practical means by which conventional crystal optics can be used in the study of crystalline materials, particularly in connection with mineralogical study, although the techniques described apply equally well to other types of crystals. Finally, some detailed explanations of certain linear optical tensors will be given.

### 1.6.2. Generalized optical, electro-optic and magneto-optic effects

When light of a particular cyclic frequency  $\omega$  is incident on a crystal of the appropriate symmetry, in general an electrical polarization  $\mathbf{P}$  may be generated within the crystal. This can be expressed in terms of a power series with respect to the electric vector of the light wave (Nussbaum & Phillips, 1976; Butcher & Cotter, 1990; Kaminow, 1974):

$$P = \sum \varepsilon_o \chi^{(i)} E^i = \varepsilon_o (\chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \dots), \quad (1.6.2.1)$$

where the  $\chi^{(i)}$  are susceptibilities of order  $i$ . Those working in the field of electro-optics tend to use this notation as a matter of course. The susceptibility  $\chi^{(1)}$  is a linear term, whereas the higher-order susceptibilities describe nonlinear behaviour.

However, it is convenient to generalize this concept to take into account other fields (*e.g.* electrical, magnetic and stress fields) that can be imposed on the crystal, not necessarily due to the incident light. The resulting polarization can be considered to arise from many different so-called electro-optic, magneto-optic and photoelastic (elasto-optic) effects, expressed as a series expansion of  $P_i$  in terms of susceptibilities  $\chi_{ijkl\dots}$  and the applied fields  $\mathbf{E}$ ,  $\mathbf{B}$  and  $T$ . This can be written in the following way:

$$\begin{aligned} P_i = & P_i^0 + \varepsilon_o \chi_{ij} E_j^\omega + \varepsilon_o \chi_{ijl} \nabla_l E_j^\omega + \varepsilon_o \chi_{ijk} E_j^{\omega_1} E_k^{\omega_2} \\ & + \varepsilon_o \chi_{ijkl} E_j^{\omega_1} E_k^{\omega_2} E_l^{\omega_3} + \varepsilon_o \chi_{ijk} E_j^{\omega_1} B_k^{\omega_2} \\ & + \varepsilon_o \chi_{ijkl} E_j^{\omega_1} B_k^{\omega_2} B_l^{\omega_3} + \varepsilon_o \chi_{ijkl} E_j^{\omega_1} T_{kl}^{\omega_2} + \dots \end{aligned} \quad (1.6.2.2)$$

Here, the superscripts refer to the frequencies of the relevant field terms and the susceptibilities are expressed as tensor components. Each term in this expansion gives rise to a specific effect that may or may not be observed, depending on the crystal symmetry and the size of the susceptibility coefficients. Note a possible confusion: in the notation  $\chi^{(i)}$ ,  $i$  is equal to one less than its rank. It is important to understand that these terms describe various properties, both linear and nonlinear. Those terms that describe the effect purely of optical frequencies propagating through the crystal give rise to *linear* and *nonlinear* optics. In the former case, the input and output frequencies are the same, whereas in the latter case, the output frequency results from sums or differences of the input frequencies. Furthermore, it is apparent that nonlinear optics depends on the intensity of the input field, and so is an effect that is induced by the strong optical field.

If the input electrical fields are static (the term ‘static’ is used here to mean zero or low frequency compared with that of light), the resulting effects are either linear or nonlinear electrical effects, in which case they are of no interest here. There is, however, an important class of effects in which both static and optical fields are involved: linear and nonlinear electro-optic effects. Here, the use of the terms linear and nonlinear is open to confusion, depending on whether it is the electrical part or the optical part to which reference is made (see for example below in the discussion of the linear electro-optic effect). Similar considerations apply to applied magnetic fields to give linear and nonlinear magneto-optic effects and to applied stresses, the *photoelastic* effects. Table 1.6.2.1 lists the most important effects according to the terms in this series. The susceptibilities are written in the form  $\chi(\omega_1; \omega_2, \omega_3, \dots)$  to indicate the frequency  $\omega_1$  of the output electric field, followed after the semicolon by the input frequencies  $\omega_1, \omega_2, \dots$

Table 1.6.2.1. Summary of linear and nonlinear optical properties

Type of polarization term	Susceptibility	Effect
$P_i^0$ $\varepsilon_o \chi_{ij} E_j^\omega$	$\chi(0; 0)$ $\chi(\omega; \omega)$	Spontaneous polarization Dielectric polarization, refractive index, linear birefringence
$\varepsilon_o \chi_{ijl} \nabla_l E_j^\omega$ $\varepsilon_o \chi_{ijk} E_j^{\omega_1} E_k^{\omega_2}$	$\chi(\omega; \omega)$ $\chi(0; 0, 0)$ $\chi(\omega; \omega, 0)$	Optical rotation (gyration) Quadratic electric effect Linear electro-optic effect or Pockels effect
	$\chi(\omega_1 \pm \omega_2; \omega_1, \omega_2)$ $\chi(\omega; \omega/2, \omega/2)$	Sum/difference frequency generation, two-wave mixing Second harmonic generation (SHG)
	$\chi(0; \omega/2, \omega/2)$ $\chi(\omega_3; \omega_1, \omega_2)$	Optical rectification Parametric amplification
$\varepsilon_o \chi_{ijkl} E_j^{\omega_1} E_k^{\omega_2} E_l^{\omega_3}$	$\chi(\omega; 0, 0)$ $\chi(\omega; \omega/2, \omega/2, 0)$	Quadratic electro-optic effect or Kerr effect Electric-field induced second harmonic generation (EFISH)
	$\chi(-\omega_1; \omega_2, \omega_3, -\omega_4)$	Four-wave mixing
$\varepsilon_o \chi_{ijk} E_j^{\omega_1} B_k^{\omega_2}$ $\varepsilon_o \chi_{ijkl} E_j^{\omega_1} B_k^{\omega_2} B_l^{\omega_3}$	$\chi(\omega; \omega, 0)$ $\chi(\omega; \omega, 0, 0)$	Faraday rotation Quadratic magneto-optic effect or Cotton-Mouton effect
$\varepsilon_o \chi_{ijkl} E_j^{\omega_1} T_{kl}^{\omega_2}$	$\chi(\omega; \omega, 0)$ $\chi(\omega_1 \pm \omega_2; \omega_1, \omega_2)$	Linear elasto-optic effect or photoelastic effect Linear acousto-optic effect

† The sudden death of Keith Cox is deeply regretted. He died in a sailing accident on 27 August 1998 in Scotland at the age of 65.

# 1. TENSORIAL ASPECTS OF PHYSICAL PROPERTIES

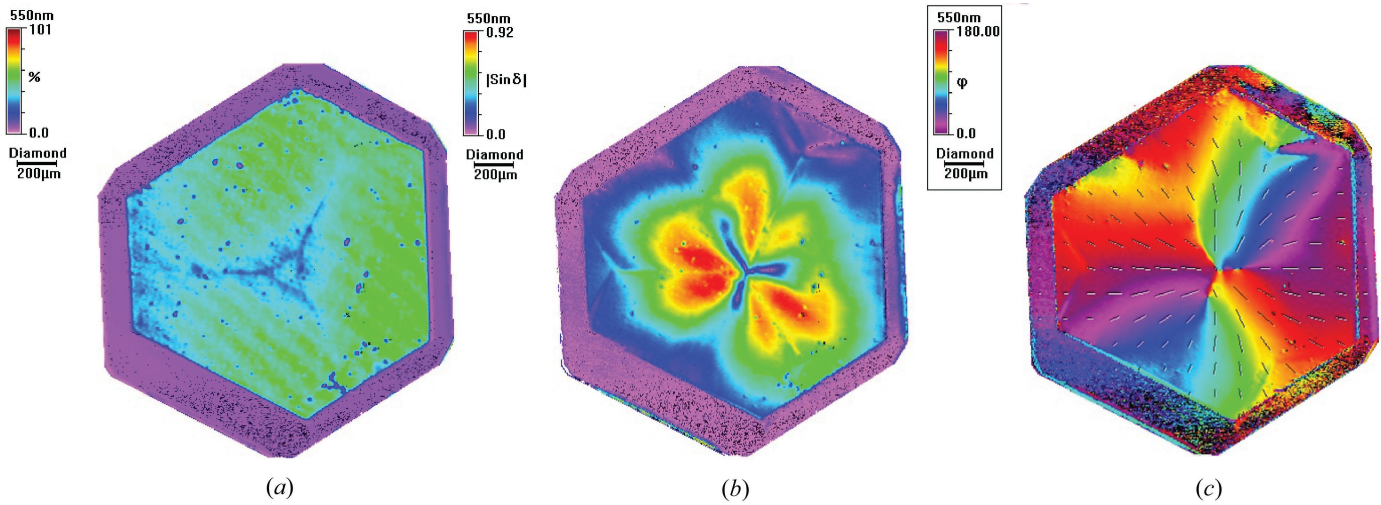


Fig. 1.6.4.7. Three birefringence images of industrial diamond viewed along [111] taken with the rotating analyser system. (a)  $I_0$ ; (b)  $|\sin \delta|$ ; (c) orientation  $\varphi$  of slow axis with respect to horizontal.

images observed in plane-polarized light rely on scattering from point sources within the specimen, and do not depend strictly on whether the configuration is conoscopic or orthoscopic. Nevertheless, relief and the Becke line are much more clearly observable in orthoscopic use.

The principle of conoscopic use is quite different. Here, the image is formed in the *back focal plane* of the objective. Any group of parallel rays passing through the specimen is brought to a focus in this plane, at a specific point depending on the direction of transmission. Hence every point in the image corresponds to a different transmission direction (see Fig. 1.6.4.8). Moreover, the visible effects are entirely caused by interference, and there is no image of the details of the specimen itself. That image is of course also present, towards the top of the tube at or near the cross wires, but the two are not simultaneously visible. The conoscopic image may be viewed simply by removing the eyepiece and looking down the tube, where it appears as a small but bright circle. More commonly however, the Bertrand lens is inserted in the tube, which has the effect of transferring the conoscopic image from the back focal plane of the objective to the front focal plane of the eyepiece, where it coincides with the cross wires and may be examined as usual.

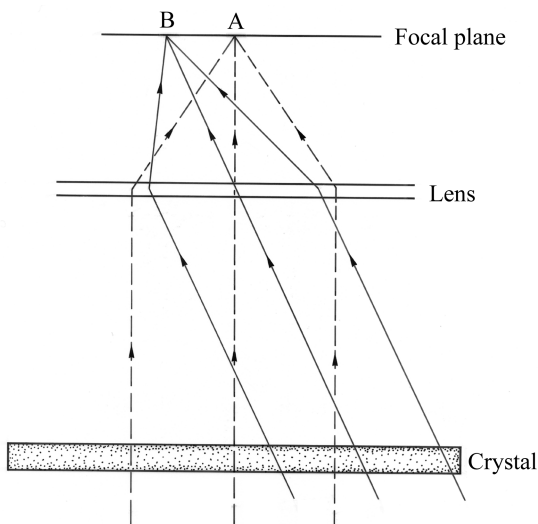


Fig. 1.6.4.8. Formation of the interference figure. The microscope axis lies vertically in the plane of the paper. A bundle of rays travelling through the crystal parallel to the microscope axis (dashed lines) is brought to a focus at A in the back focal plane of the objective. This is the centre of the interference figure. A bundle of oblique rays (solid lines) is brought to a focus at B, towards the edge of the figure.

It is useful to think of the conoscopic image as analogous to the gnomonic projection as used in crystallography. The geometrical principles are the same, as each direction through the crystal is projected directly through the centre of the lens into the back focal plane.

## 1.6.4.12. Uniaxial figures

To understand the formation of an interference figure, consider a simple example, a specimen of calcite cut at right angles to the  $c$  crystallographic axis. Calcite is uniaxial negative, with the optic axis parallel to  $c$ . The rays that have passed most obliquely through the specimen are focused around the edge of the figure, while the centre is occupied by rays that have travelled parallel to the optic axis (see Fig. 1.6.4.8). The birefringence within the image clearly must increase from nil in the centre to some higher value at the edges, because the rays here have had longer path lengths through the crystal. Furthermore, the image must have radial symmetry, so that the first most obvious feature of the figure is a series of coloured rings, corresponding in outward sequence to the successive orders. The number of rings visible will of course depend on the thickness of the sample, and when birefringence is low enough no rings will be obvious because all colours lie well within the first order (Figs. 1.6.4.9a and b). Fig. 1.6.4.10(a) illustrates, by reference to the indicatrix, the way in which the vibration directions of the  $o$  and  $e$  rays are disposed. Fig. 1.6.4.10(b) shows the disposition of vibration directions in the figure. Note that  $o$  rays always vibrate tangentially and  $e$  rays radially. The  $o$ -ray vibration directions lie in the plane of the figure, but  $e$ -ray vibration directions become progressively more inclined to the plane of the figure towards the edge.

The shaded cross on the figure illustrates the position of dark 'brushes' known as *isogyres* (Fig. 1.6.4.10b). These develop wherever vibration directions lie N-S or E-W, hence corresponding to the vibration directions of the analyser and polarizer. As the stage is rotated, as long as the optic axis is truly parallel to the microscope axis, the figure will not change. This is an example of a centred uniaxial optic axis figure, and such a figure identifies the crystal as belonging to the tetragonal, trigonal or hexagonal systems (see Fig. 1.6.4.11a).

From the point of crystal identification, one can also determine whether the figure coincides with the uniaxial positive ( $n_e > n_o$ ) or uniaxial negative ( $n_e < n_o$ ) cases. Inserting the sensitive-tint plate will move the coloured ring up or down the birefringence scale by a complete order. Fig. 1.6.4.11(c) shows the centred optic axis figure for calcite, which is optically negative. The insertion of a tint plate with its slow vibration direction lying NE-SW lowers the colours in the NE and SW quadrants of the figure, and raises

## 1.7. Nonlinear optical properties

BY B. BOULANGER AND J. ZYSS

### 1.7.1. Introduction

The first nonlinear optical phenomenon was observed by Franken *et al.* (1961): ultraviolet radiation at 0.3471  $\mu\text{m}$  was detected at the exit of a quartz crystal illuminated with a ruby laser beam at 0.6942  $\mu\text{m}$ . This was the first demonstration of second harmonic generation at optical wavelengths. A coherent light of a few  $\text{W cm}^{-2}$  is necessary for the observation of nonlinear optical interactions, which thus requires the use of laser beams.

The basis of nonlinear optics, including quantum-mechanical perturbation theory and Maxwell equations, is given in the paper published by Armstrong *et al.* (1962).

It would take too long here to give a complete historical account of nonlinear optics, because it involves an impressive range of different aspects, from theory to applications, from physics to chemistry, from microscopic to macroscopic aspects, from quantum mechanics of materials to classical and quantum electrodynamics, from gases to solids, from mineral to organic compounds, from bulk to surface, from waveguides to fibres and so on.

Among the main nonlinear optical effects are harmonic generation, parametric wave mixing, stimulated Raman scattering, self-focusing, multiphoton absorption, optical bistability, phase conjugation and optical solitons.

This chapter deals mainly with harmonic generation and parametric interactions in anisotropic crystals, which stand out as one of the most important fields in nonlinear optics and certainly one of its oldest and most rigorously treated topics. Indeed, there is a great deal of interest in the development of solid-state laser sources, be they tunable or not, in the ultraviolet, visible and infrared ranges. Spectroscopy, telecommunications, telemetry and optical storage are some of the numerous applications.

The electric field of light interacts with the electric field of matter by inducing a dipole due to the displacement of the electron density away from its equilibrium position. The induced dipole moment is termed polarization and is a vector: it is related to the applied electric field *via* the dielectric susceptibility tensor. For fields with small to moderate amplitude, the polarization remains linearly proportional to the field magnitude and defines the linear optical properties. For increasing field amplitudes, the polarization is a nonlinear function of the applied electric field and gives rise to nonlinear optical effects. The polarization is properly modelled by a Taylor power series of the applied electric field if its strength does not exceed the atomic electric field ( $10^8$ – $10^9$   $\text{V cm}^{-1}$ ) and if the frequency of the electric field is far away from the resonance frequencies of matter. Our purpose lies within this framework because it encompasses the most frequently encountered cases, in which laser intensities remain in the kW to MW per  $\text{cm}^2$  range, that is to say with electric fields from  $10^3$  to  $10^4$   $\text{V cm}^{-1}$ . The electric field products appearing in the Taylor series express the interactions of different optical waves. Indeed, a wave at the circular frequency  $\omega$  can be radiated by the second-order polarization induced by two waves at  $\omega_a$  and  $\omega_b$  such as  $\omega = \omega_a \pm \omega_b$ : these interactions correspond to sum-frequency generation ( $\omega = \omega_a + \omega_b$ ), with the particular cases of second harmonic generation ( $2\omega_a = \omega_a + \omega_a$ ) and indirect third harmonic generation ( $3\omega_a = \omega_a + 2\omega_a$ ); the other three-wave process is difference-frequency generation, including optical parametric amplification and optical parametric oscillation. In the same way, the third-order polarization governs four-wave mixing: direct third harmonic generation ( $3\omega_a = \omega_a + \omega_a + \omega_a$ )

and more generally sum- and difference-frequency generations ( $\omega = \omega_a \pm \omega_b \pm \omega_c$ ).

Here, we do not consider optical interactions at the microscopic level, and we ignore the way in which the atomic or molecular dielectric susceptibility determines the macroscopic optical properties. Microscopic solid-state considerations and the relations between microscopic and macroscopic optical properties, particularly successful in the realm of organic crystals, play a considerable role in materials engineering and optimization. This important topic, known as molecular and crystalline engineering, lies beyond the scope of this chapter. Therefore, all the phenomena studied here are connected to the macroscopic first-, second- and third-order dielectric susceptibility tensors  $\chi^{(1)}$ ,  $\chi^{(2)}$  and  $\chi^{(3)}$ , respectively; we give these tensors for all the crystal point groups.

We shall mainly emphasize propagation aspects, on the basis of Maxwell equations which are expressed for each Fourier component of the optical field in the nonlinear crystal. The reader will then follow how the linear optical properties come to play a pivotal role in the nonlinear optical interactions. Indeed, an efficient quadratic or cubic interaction requires not only a high magnitude of  $\chi^{(2)}$  or  $\chi^{(3)}$ , respectively, but also specific conditions governed by  $\chi^{(1)}$ : existence of phase matching between the induced nonlinear polarization and the radiated wave; suitable symmetry of the field tensor, which is defined by the tensor product of the electric field vectors of the interacting waves; and small or nil double refraction angles. Quadratic and cubic processes cannot be considered as fully independent in the context of cascading. Significant phase shifts driven by a sequence of sum- and difference-frequency generation processes attached to a  $\chi^{(2)} \cdot \chi^{(2)}$  contracted tensor expression have been reported (Bosshard, 2000). These results point out the relevance of polar structures to cubic phenomena in both inorganic and organic structures, thus somewhat blurring the borders between quadratic and cubic NLO.

We analyse in detail second harmonic generation, which is the prototypical interaction of frequency conversion. We also present indirect and direct third harmonic generations, sum-frequency generation and difference-frequency generation, with the specific cases of optical parametric amplification and optical parametric oscillation.

An overview of the methods of measurement of the nonlinear optical properties is provided, and the chapter concludes with a comparison of the main mineral and organic crystals showing nonlinear optical properties.

### 1.7.2. Origin and symmetry of optical nonlinearities

#### 1.7.2.1. Induced polarization and susceptibility

The macroscopic electronic polarization of a unit volume of the material system is classically expanded in a Taylor power series of the applied electric field  $\mathbf{E}$ , according to Bloembergen (1965):

$$\mathbf{P} = \mathbf{P}_0 + \varepsilon_o(\chi^{(1)} \cdot \mathbf{E} + \chi^{(2)} \cdot \mathbf{E}^2 + \dots + \chi^{(n)} \cdot \mathbf{E}^n + \dots), \quad (1.7.2.1)$$

where  $\chi^{(n)}$  is a tensor of rank  $n + 1$ ,  $\mathbf{E}^n$  is a shorthand abbreviation for the  $n$ th order tensor product  $\mathbf{E} \otimes \mathbf{E} \otimes \dots \otimes \mathbf{E} = \otimes^n \mathbf{E}$  and the dot stands for the contraction of the last  $n$  indices of the

## 1.7. NONLINEAR OPTICAL PROPERTIES

Table 1.7.3.9. Field-tensor components specifically nil in the principal planes of uniaxial and biaxial crystals for three-wave and four-wave interactions

( $i, j, k$ ) =  $x, y$  or  $z$ .

Configurations of polarization	Nil field-tensor components		
	(xy) plane	(xz) plane	(yz) plane
<i>ooo</i>	$F_{xjk} = 0; F_{yjk} = 0$	$F_{ixk} = F_{ijx} = 0$ $F_{yjk} = 0$	$F_{iyk} = F_{ijy} = 0$ $F_{xjk} = 0$
<i>oeo</i>	$F_{ixk} = F_{ijx} = 0$ $F_{iyk} = F_{ijy} = 0$	$F_{iyk} = F_{ijy} = 0$ $F_{xik} = 0$	$F_{ixk} = F_{ijx} = 0$ $F_{yjk} = 0$
<i>ooo</i>	$F_{xjkl} = 0; F_{yjkl} = 0$	$F_{ixkl} = F_{ijxl} = F_{ijkx} = 0$ $F_{yjkl} = 0$	$F_{iykl} = F_{ijyl} = F_{ijkx} = 0$ $F_{xjkl} = 0$
<i>oeoe</i>	$F_{ixkl} = F_{ijxl} = F_{ijkx} = 0$ $F_{iykl} = F_{ijyl} = F_{ijkx} = 0$	$F_{iykl} = F_{ijyl} = F_{ijkx} = 0$ $F_{xjkl} = 0$	$F_{ixkl} = F_{ijxl} = F_{ijkx} = 0$ $F_{yjkl} = 0$
<i>ooee</i>	$F_{ixkl} = F_{ijkx} = 0$ $F_{ijyl} = F_{ijkx} = 0$	$F_{xjkl} = F_{ijkx} = 0$ $F_{ijyl} = F_{ijkx} = 0$	$F_{iykl} = F_{ijkx} = 0$ $F_{ijxl} = F_{ijkx} = 0$

and configurations of polarization:  $D_4$  and  $D_6$  for  $2o.e$ ,  $C_{4v}$  and  $C_{6v}$  for  $2e.o$ ,  $D_6$ ,  $D_{6h}$ ,  $D_{3h}$  and  $C_{6v}$  for  $3o.e$  and  $3e.o$ . Thus, even if phase-matching directions exist, the effective coefficient in these situations is nil, which forbids the interactions considered (Boulanger & Marnier, 1991; Boulanger *et al.*, 1993). The number of forbidden crystal classes is greater under the Kleinman approximation. The forbidden crystal classes have been determined for the particular case of third harmonic generation assuming Kleinman conjecture and without consideration of the field tensor (Midwinter & Warner, 1965).

### 1.7.3.2.4.3. Biaxial class

The symmetry of the biaxial field tensors is the same as for the uniaxial class, though only for a propagation in the principal planes  $xz$  and  $yz$ ; the associated matrix representations are given in Tables 1.7.3.7 and 1.7.3.8, and the nil components are listed in Table 1.7.3.9. Because of the change of optic sign from either side of the optic axis, the field tensors of the interactions for which the phase-matching cone joins areas  $b$  and  $a$  or  $a$  and  $c$ , given in Fig. 1.7.3.5, change from one area to another: for example, the field tensor (*oeoe*) becomes an (*ooeo*) and so the solicited components of the electric susceptibility tensor are not the same.

The nonzero field-tensor components for a propagation in the  $xy$  plane of a biaxial crystal are:  $F_{zxx}, F_{zyy}, F_{zxy} \neq F_{zyx}$  for (*ooo*);  $F_{xzz}, F_{yzz}$  for (*oeo*);  $F_{zxxx}, F_{zyyy}, F_{zxyy} \neq F_{zyyx} \neq F_{zyxx}, F_{zxyx} \neq F_{zyyx} \neq F_{zyxx}$  for (*ooo*);  $F_{xzzz}, F_{yzzz}$  for (*oeoe*);  $F_{xyzz} \neq F_{yxzz}, F_{xxzz}, F_{yyzz}$  for (*ooee*). The nonzero components for the other configurations of polarization are obtained by the associated permutations of the Cartesian indices and the corresponding polarizations.

The field tensors are not symmetric for a propagation out of the principal planes in the general case where all the frequencies are different: in this case there are 27 independent components for the three-wave interactions and 81 for the four-wave interactions, and so all the electric susceptibility tensor components are solicited.

As phase matching imposes the directions of the electric fields of the interacting waves, it also determines the field tensor and hence the effective coefficient. Thus there is no possibility of choice of the  $\chi^{(2)}$  coefficients, since a given type of phase matching is considered. In general, the largest coefficients of polar crystals, *i.e.*  $\chi_{zzz}$ , are implicated at a very low level when phase matching is achieved, because the corresponding field tensor, *i.e.*  $F_{zzz}$ , is often weak (Boulanger *et al.*, 1997). In contrast, QPM authorizes the coupling between three waves polarized along the  $z$  axis, which leads to an effective coefficient which is purely  $\chi_{zzz}$ , *i.e.*  $\chi_{\text{eff}} = (2/\pi)\chi_{zzz}$ , where the numerical factor comes from the periodic character of the rectangular function of modulation (Fejer *et al.*, 1992).

### 1.7.3.3. Integration of the propagation equations

#### 1.7.3.3.1. Spatial and temporal profiles

The resolution of the coupled equations (1.7.3.22) or (1.7.3.24) over the crystal length  $L$  leads to the electric field amplitude  $E_i(X, Y, L)$  of each interacting wave. The general solutions are Jacobian elliptic functions (Armstrong *et al.*, 1962; Fève, Boulanger & Douady, 2002). The integration of the systems is simplified for cases where one or several beams are held constant, which is called the undepleted pump approximation. We consider mainly this kind of situation here. The power of each interacting wave is calculated by integrating the intensity over the cross section of each beam according to (1.7.3.8). For our main purpose, we consider the simple case of plane-wave beams with two kinds of transverse profile:

$$\begin{aligned} \mathbf{E}(X, Y, Z) &= \mathbf{e}E_o(Z) & \text{for } (X, Y) \in [-w_o, +w_o] \\ \mathbf{E}(X, Y, Z) &= 0 & \text{elsewhere} \end{aligned} \quad (1.7.3.36)$$

for a flat distribution over a radius  $w_o$ ;

$$\mathbf{E}(X, Y, Z) = \mathbf{e}E_o(Z) \exp[-(X^2 + Y^2)/w_o^2] \quad (1.7.3.37)$$

for a Gaussian distribution, where  $w_o$  is the radius at  $(1/e)$  of the electric field and so at  $(1/e^2)$  of the intensity.

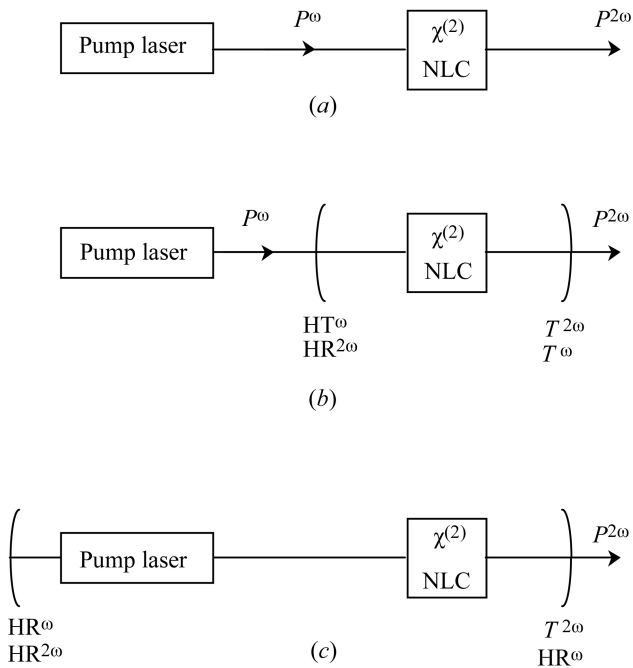


Fig. 1.7.3.6. Schematic configurations for second harmonic generation. (a) Non-resonant SHG; (b) external resonant SHG: the resonant wave may either be the fundamental or the harmonic one; (c) internal resonant SHG.  $P^{\omega, 2\omega}$  are the fundamental and harmonic powers;  $HT^{\omega}$  and  $HR^{\omega, 2\omega}$  are the high-transmission and high-reflection mirrors at  $\omega$  or  $2\omega$  and  $T^{\omega, 2\omega}$  are the transmission coefficients of the output mirror at  $\omega$  or  $2\omega$ . NLC is the nonlinear crystal with a nonzero  $\chi^{(2)}$ .

## 1.8. TRANSPORT PROPERTIES

$$\rho(T) = \rho_i(1 + BT^2) + AT^2. \quad (1.8.3.14)$$

The term  $\rho_i$  is the constant due to the impurity scattering. There is also a term proportional to  $BT^2$ , which is proportional to the impurity resistance. This factor is due to the Koshino–Taylor effect (Koshino, 1960; Taylor, 1964), which has been treated rigorously by Mahan & Wang (1989). It is the inelastic scattering of electrons by impurities. The impurity is part of the lattice and phonons can be excited when the impurity scatters the electrons. The term  $AT^2$  is due to electron–electron interactions. The Coulomb interaction between electrons is highly screened and makes only a small contribution to  $A$ . The largest contribution to  $A$  is caused by phonons. MacDonald *et al.* (1981) showed that electrons can interact by exchanging phonons. There are also terms due to boundary scattering, which is important in thin films: see Bruls *et al.* (1985).

Note that (1.8.3.14) has no term from phonons of  $O(T^5)$ . Such a term is lacking in simple metals, contrary to the assertion in most textbooks. Its absence is due to *phonon drag*. For a review and explanation of this behaviour, see Wiser (1984). The  $T^5$  term is found in the noble metals, where phonon drag is less important owing to the complexities of the Fermi surface.

### 1.8.3.2. Metal alloys

Alloys are solids composed of a mixture of two or more elements that do not form a stoichiometric compound. An example is  $\text{Cu}_x\text{Ni}_{1-x}$ , in which  $x$  can have any value. For small values of  $x$ , or of  $(1-x)$ , the atoms of one element just serve as impurities in the other element. This results in the type of behaviour described above. However, in the range  $0.2 < x < 0.8$ , a different type of resistivity is found. This was first summarized by Mooij (1973), who found a remarkable range of behaviours. He measured the resistivity of hundreds of alloys and also surveyed the published literature for additional results. He represented the resistivity at  $T = 300$  K by two values: the resistivity itself,  $\rho(T = 300)$ , and its logarithmic derivative,  $\alpha = d \ln(\rho)/dT$ . He produced the graph shown in Fig. 1.8.3.2, where these two values are plotted against each other. Each point is one sample as represented by these two numbers. He found that all of the results fit within a band of numbers, in which larger values of  $\rho(T = 300)$  are accompanied by negative values of  $\alpha$ . Alloys with very high values of resistivity generally have a resistivity  $\rho(T)$  that decreases with increasing temperature. The region where  $\alpha = 0$  corresponds to a resistivity of  $\rho^* = 150 \mu\Omega \text{ cm}$ , which appears to be a fixed point. As the temperature is increased, the resistivities of alloys with  $\rho > \rho^*$  decrease to this value, while the resistivities of alloys with  $\rho < \rho^*$  increase to this value.

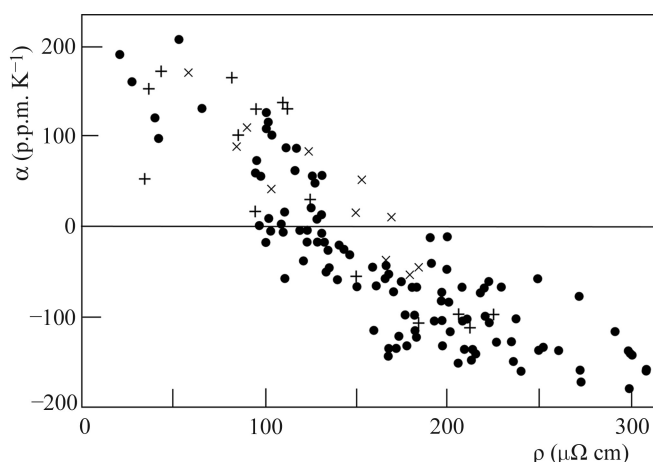


Fig. 1.8.3.2. The temperature coefficient of resistance *versus* resistivity for alloys according to Mooij (1973). Data are shown for bulk alloys (+), thin films (•) and amorphous alloys (x).

Mooij's observations are obviously important, but the reason for this behaviour is not certain. Several different explanations have been proposed and all are plausible: see Jonson & Girvin (1979), Allen & Chakraborty (1981) or Tsuei (1986).

Recently, another group of alloys have been found that are called *bad metals*. The ruthenates (see Allen *et al.*, 1996; Klein *et al.*, 1996) have a resistivity  $\rho > \rho^*$  that increases at high temperatures. Their values are outliers on Mooij's plot.

### 1.8.3.3. Semiconductors

The resistivity of semiconductors varies from sample to sample, even of the same material. The conductivity can be written as  $\sigma = n_0 e \mu$ , where  $e$  is the charge on the electron,  $\mu = e\tau/m^*$  is the mobility and  $n_0$  is the density of conducting particles (electrons or holes). It is the density of particles  $n_0$  that varies from sample to sample. It depends upon the impurity content of the semiconductor as well as upon temperature. Since no two samples have exactly the same number of impurities, they do not have the same values of  $n_0$ . In semiconductors and insulators, the conducting particles are extrinsic – they come from defects, impurities or thermal excitation – in contrast to metals, where the density of the conducting electrons is usually an intrinsic property.

In semiconductors, instead of talking about the conductivity, the more fundamental transport quantity (Rode, 1975) is the mobility  $\mu$ . It is the same for each sample at high temperature if the density of impurities and defects is low. There is an intrinsic mobility, which can be calculated assuming there are no impurities and can be measured in samples with a very low density of impurities. We shall discuss the intrinsic mobility first.

Fig. 1.8.3.3 shows the intrinsic mobility of electrons in silicon, from Rode (1972), as a function of temperature. The mobility generally decreases with increasing temperature. This behaviour is found in all common semiconductors. The mobility also decreases with an increasing concentration of impurities: see Jacoboni *et al.* (1977).

The intrinsic mobility of semiconductors is due to the scattering of electrons and holes by phonons. The phonons come in various branches called TA, LA, TO and LO, where T is transverse, L is longitudinal, A is acoustic and O is optical. At long wavelengths, the acoustic modes are just the sound waves, which

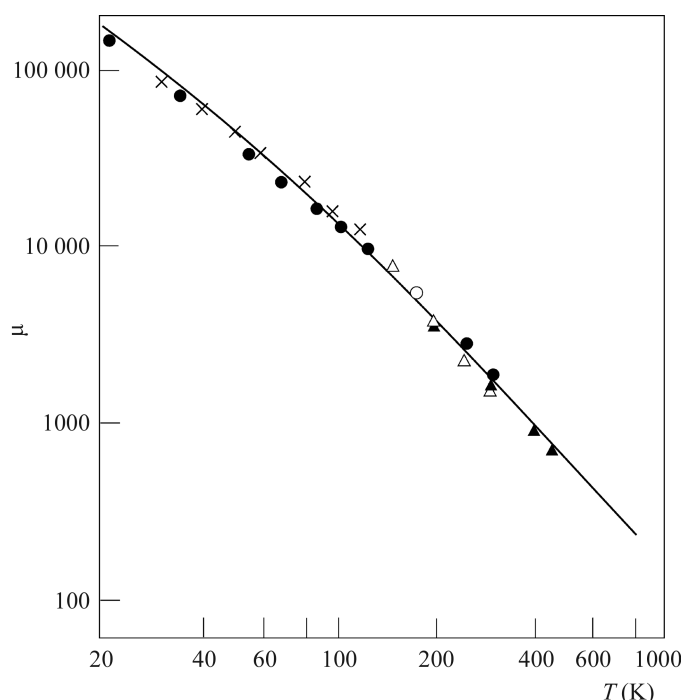


Fig. 1.8.3.3. The intrinsic mobility of electrons in silicon. Solid line: theory; points: experimental. After Rode (1972).

## 1.9. Atomic displacement parameters

BY W. F. KUHS

### 1.9.1. Introduction

Atomic thermal motion and positional disorder is at the origin of a systematic intensity reduction of Bragg reflections as a function of scattering vector  $\mathbf{Q}$ . The intensity reduction is given as the well known *Debye–Waller factor* (DWF); the DWF may be of purely thermal origin (*thermal DWF* or *temperature factor*) or it may contain contributions of static atomic disorder (*static DWF*). As atoms of chemically or isotopically different elements behave differently, the individual atomic contributions to the global DWF (describing the weakening of Bragg intensities) vary. Formally, one may split the global DWF into the individual atomic contributions. Crystallographic experiments usually measure the global weakening of Bragg intensities and the individual contributions have to be assessed by adjusting individual atomic parameters in a least-squares refinement.

The theory of lattice dynamics (see *e.g.* Willis & Pryor, 1975) shows that the atomic thermal DWF  $T_\alpha$  is given by an exponential of the form

$$T_\alpha(\mathbf{Q}) = \langle \exp(i\mathbf{Q}\mathbf{u}_\alpha) \rangle, \quad (1.9.1.1)$$

where  $\mathbf{u}_\alpha$  are the individual atomic displacement vectors and the brackets symbolize the thermodynamic (time–space) average over all contributions  $\mathbf{u}_\alpha$ . In the harmonic (Gaussian) approximation, (1.9.1.1) reduces to

$$T_\alpha(\mathbf{Q}) = \exp[(-1/2)\langle (\mathbf{Q}\mathbf{u}_\alpha)^2 \rangle]. \quad (1.9.1.2)$$

The thermodynamically averaged atomic mean-square displacements (of thermal origin) are given as  $U^{ij} = \langle u^i u^j \rangle$ , *i.e.* they are the thermodynamic average of the product of the displacements along the  $i$  and  $j$  coordinate directions. Thus (1.9.1.2) may be expressed with  $\mathbf{Q} = 4\pi\mathbf{h}|\mathbf{a}|$  in a form more familiar to the crystallographer as

$$T_\alpha(\mathbf{h}) = \exp(-2\pi^2 h_i |\mathbf{a}^i| h_j |\mathbf{a}^j| U_\alpha^{ij}), \quad (1.9.1.3)$$

where  $h_i$  are the covariant Miller indices,  $\mathbf{a}^i$  are the reciprocal-cell basis vectors and  $1 \leq i, j \leq 3$ . Here and in the following, tensor notation is employed; implicit summation over repeated indices is assumed unless stated otherwise. For computational convenience one often writes

$$T_\alpha(\mathbf{h}) = \exp(-h_i h_j \beta_\alpha^{ij}) \quad (1.9.1.4)$$

with  $\beta_\alpha^{ij} = 2\pi^2 |\mathbf{a}^i| |\mathbf{a}^j| U_\alpha^{ij}$  (no summation). Both  $\mathbf{h}$  and  $\beta$  are dimensionless tensorial quantities;  $\mathbf{h}$  transforms as a covariant tensor of rank 1,  $\beta$  as a contravariant tensor of rank 2 (for details of the mathematical notion of a tensor, see Chapter 1.1).

Similar formulations are found for the static atomic DWF  $S_\alpha$ , where the average of the atomic static displacements  $\Delta\mathbf{u}_\alpha$  may also be approximated [though with weaker theoretical justification, see Kuhs (1992)] by a Gaussian distribution:

$$S_\alpha(\mathbf{Q}) = \exp[(-1/2)\langle (\mathbf{Q}\Delta\mathbf{u}_\alpha)^2 \rangle]. \quad (1.9.1.5)$$

As in equation (1.9.1.3), the static atomic DWF may be formulated with the mean-square disorder displacements  $\Delta U^{ij} = \langle \Delta u^i \Delta u^j \rangle$  as

$$S_\alpha(\mathbf{h}) = \exp(-2\pi^2 h_i |\mathbf{a}^i| h_j |\mathbf{a}^j| \Delta U_\alpha^{ij}). \quad (1.9.1.6)$$

It is usually difficult to separate thermal and static contributions, and it is often wise to use the sum of both and call them simply (mean-square) atomic displacements. A separation may however be achieved by a temperature-dependent study of atomic displacements. A harmonic diagonal tensor component of purely thermal origin extrapolates linearly to zero at 0 K; zero-point motion causes a deviation from this linear behaviour at low temperatures, but an extrapolation from higher temperatures (where the contribution from zero-point motion becomes negligibly small) still yields a zero intercept. Any positive intercept in such extrapolations is then due to a (temperature-independent) static contribution to the total atomic displacements. Care has to be taken in such extrapolations, as pronounced anharmonicity (frequently encountered at temperatures higher than the Debye temperature) will change the slope, thus invalidating the linear extrapolation (see *e.g.* Willis & Pryor, 1975). Owing to the difficulty in separating thermal and static displacements in a standard crystallographic structure analysis, a subcommittee of the IUCr Commission on Crystallographic Nomenclature has recommended the use of the term *atomic displacement parameters* (ADPs) for  $U^{ij}$  and  $\beta^{ij}$  (Trueblood *et al.*, 1996).

### 1.9.2. The atomic displacement parameters (ADPs)

One notes that in the Gaussian approximation, the mean-square atomic displacements (composed of thermal and static contributions) are fully described by six coefficients  $\beta^{ij}$ , which transform on a change of the direct-lattice base (according to  $\mathbf{a}_k = A_{ki}\mathbf{a}_i$ ) as

$$\beta^{kl} = A_{ki} A_{lj} \beta^{ij}. \quad (1.9.2.1)$$

This is the transformation law of a tensor (see Section 1.1.3.2); the mean-square atomic displacements are thus tensorial properties of an atom  $\alpha$ . As the tensor is contravariant and in general is described in a (non-Cartesian) crystallographic basis system, its indices are written as superscripts. It is convenient for comparison purposes to quote the dimensionless coefficients  $\beta^{ij}$  as their dimensioned representations  $U^{ij}$ .

In the harmonic approximation, the atomic displacements are fully described by the fully symmetric second-order tensor given in (1.9.2.1). Anharmonicity and disorder, however, cause deviations from a Gaussian distribution of the atomic displacements around the atomic position. In fact, anharmonicity in the thermal motion also provokes a shift of the atomic position as a function of temperature. A generalized description of atomic displacements therefore also involves first-, third-, fourth- and even higher-order displacement terms. These terms are defined by a moment-generating function  $M(\mathbf{Q})$  which expresses  $\langle \exp(i\mathbf{Q}\mathbf{u}_\alpha) \rangle$  in terms of an infinite number of moments; for a Gaussian distribution of displacement vectors, all moments of order  $> 2$  are identically equal to zero. Thus

$$M(\mathbf{Q}) = \langle \exp(i\mathbf{Q}\mathbf{u}_\alpha) \rangle = \sum_{N=0}^{\infty} (i^N / N!) \langle (\mathbf{Q}\mathbf{u}_\alpha)^N \rangle. \quad (1.9.2.2)$$

The moments  $\langle (\mathbf{Q}\mathbf{u}_\alpha)^N \rangle$  of order  $N$  may be expressed in terms of cumulants  $\langle (\mathbf{Q}\mathbf{u}_\alpha)^N \rangle_{\text{cum}}$  by the identity

$$\sum_{N=0}^{\infty} (1/N!) \langle (\mathbf{Q}\mathbf{u}_\alpha)^N \rangle \equiv \exp \sum_{N=1}^{\infty} (1/N!) \langle (\mathbf{Q}\mathbf{u}_\alpha)^N \rangle_{\text{cum}}. \quad (1.9.2.3)$$

## 1.9. ATOMIC DISPLACEMENT PARAMETERS

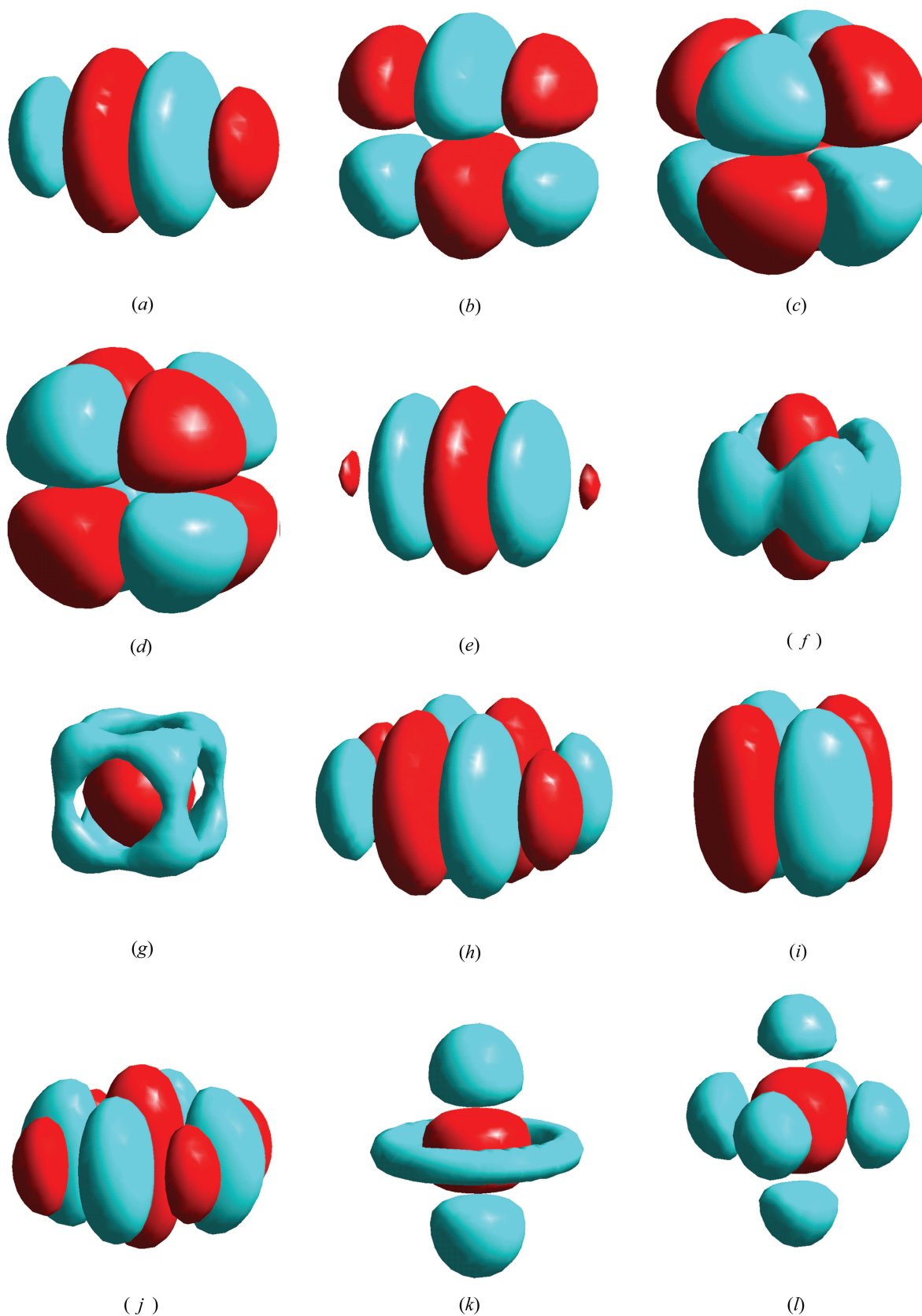


Fig. 1.9.4.1. A selection of graphical representations of density modulations due to higher-order terms in the Gram-Charlier series expansion of a Gaussian atomic probability density function. All figures are drawn on a common scale and have a common orientation. All terms within any given order of expansion are numerically identical and refer to the same underlying isotropic second-order term; the higher-order terms of different order of expansion differ by one order of magnitude, but refer again to the same underlying isotropic second-order term. The orthonormal crystallographic axes are oriented as follows:  $x$  oblique out of the plane of the paper towards the observer,  $y$  in the plane of the paper and to the right, and  $z$  in the plane of the paper and upwards. All surfaces are scaled to 1% of the absolute value of the maximum modulation within each density distribution. Positive modulations (*i.e.* an increase of density) are shown in red, negative modulations are shown in blue. The source of illumination is located approximately on the  $[111]$  axis. The following graphs are shown (with typical point groups for specific cases given in parentheses). Third-order terms: (a)  $b^{222}$ ; (b)  $b^{223}$ ; (c)  $b^{113} = -b^{223}$  (point group  $\bar{4}$ ); (d)  $b^{123}$  (point group  $43m$ ). Fourth-order terms: (e)  $b^{2222}$ ; (f)  $b^{1111} = b^{2222}$ ; (g)  $b^{1111} = b^{2222} = b^{3333}$  (point group  $m\bar{3}m$ ); (h)  $b^{1222}$ ; (i)  $b^{1112} = b^{1222}$ ; (j)  $b^{1122}$ ; (k)  $b^{1153} = b^{2233}$ ; (l)  $b^{1122} = b^{1153} = b^{2233}$  (point group  $m\bar{3}m$ ).

## 1.10. Tensors in quasiperiodic structures

BY T. JANSSEN

### 1.10.1. Quasiperiodic structures

#### 1.10.1.1. Introduction

Many materials are known which show a well ordered state without lattice translation symmetry, often in a restricted temperature or composition range. This can be seen in the diffraction pattern from the appearance of sharp spots that cannot be labelled in the usual way with three integer indices. The widths of the peaks are comparable with those of perfect lattice periodic crystals, and this is a sign that the coherence length is comparable as well.

A typical example is  $\text{K}_2\text{SeO}_4$ , which has a normal lattice periodic structure above 128 K with space group  $Pcmm$ , but below this temperature shows satellites at positions  $\gamma\mathbf{c}^*$ , where  $\gamma$  is an irrational number, which in addition depends on temperature. These satellites cannot be labelled with integer indices with respect to the reciprocal basis  $\mathbf{a}^*$ ,  $\mathbf{b}^*$ ,  $\mathbf{c}^*$  of the structure above the transition temperature. Therefore, the corresponding structure cannot be lattice periodic.

The diffraction pattern of  $\text{K}_2\text{SeO}_4$  arises because the original lattice periodic *basic structure* is deformed below 128 K. The atoms are displaced from their positions in the basic structure such that the displacement itself is again periodic, but with a period that is *incommensurate* with respect to the lattice of the basic structure.

Such a *modulated structure* is just a special case of a more general type of structure. These structures are characterized by the fact that the diffraction pattern has sharp Bragg peaks at positions  $\mathbf{H}$  that are linear combinations of a finite number of basic vectors:

$$\mathbf{H} = \sum_{i=1}^n h_i \mathbf{a}_i^* \quad (\text{integer } h_i). \quad (1.10.1.1)$$

Structures that have this property are called *quasiperiodic*. The minimal number  $n$  of basis vectors such that all  $h_i$  are integers is called the *rank* of the structure. If the rank is three and the vectors  $\mathbf{a}_i$  do not all fall on a line or in a plane, the structure is just lattice periodic. Lattice periodic structures form special cases of quasiperiodic structures. The collection of vectors  $\mathbf{H}$  forms the *Fourier module* of the structure. For rank three, this is just the *reciprocal lattice* of the lattice periodic structure.

The definition given above results in some important practical difficulties. In the first place, it is not possible to show experimentally that a wavevector has irrational components instead of rational ones, because an irrational number can be approximated by a rational number arbitrarily well. Very often the wavevector of the satellite changes with temperature. It has been reported that in some compounds the variation shows plateaux, but even when the change seems to be continuous and smooth one can not be sure about the irrationality. On the other hand, if the wavevector jumps from one rational position to another, the structure would always be lattice periodic, but the unit cell of this structure would vary wildly with temperature. This means that, if one wishes to describe the incommensurate phases in a unified fashion, it is more convenient to treat the wavevector as generically irrational. This experimental situation is by no means dramatic. It is similar to the way in which one can never be sure that the angles between the basis vectors of an orthorhombic lattice are really  $90^\circ$ , although this is a concept that no-one has problems in understanding.

A second problem stems from the fact that the wavevectors of the Fourier module are dense. For example, in the case of  $\text{K}_2\text{SeO}_4$  the linear combinations of  $\mathbf{c}^*$  and  $\gamma\mathbf{c}^*$  cover the  $c$  axis uniformly. To pick out a basis here could be problematic, but the intensity of the spots is usually such that choosing a basis is not a problem. In fact, one only observes peaks with an intensity above a certain threshold, and these form a discrete set. At most, the occurrence of scale symmetry may make the choice less obvious.

#### 1.10.1.2. Types of quasiperiodic crystals

One may distinguish various families of quasiperiodic systems. [Sometimes these are also called incommensurate systems if they are not lattice periodic (Janssen & Janner, 1987).] It is not a strict classification, because one may have intermediate cases belonging to more than one family as well. Here we shall consider a number of pure cases.

An *incommensurately modulated structure* or *incommensurate crystal (IC)* phase is a periodically modified structure that without the modification would be lattice periodic. Hence there is a *basic structure* with space-group symmetry. The periodicity of the modification should be incommensurate with respect to the basic structure. The position of the  $j$ th atom in the unit cell with origin at the lattice point  $\mathbf{n}$  is  $\mathbf{n} + \mathbf{r}_j$  ( $j = 1, 2, \dots, s$ ).

For a *displacive modulation*, the positions of the atoms are shifted from a lattice periodic basic structure. A simple example is a structure that can be derived from the positions of the basic structure with a simple displacement wave. The positions of the atoms in the IC phase are then

$$\mathbf{n} + \mathbf{r}_j + \mathbf{f}_j(\mathbf{Q} \cdot \mathbf{n}) \quad [\mathbf{f}_j(x) = \mathbf{f}_j(x + 1)]. \quad (1.10.1.2)$$

Here the *modulation wavevector*  $\mathbf{Q}$  has irrational components with respect to the reciprocal lattice of the basic structure. One has

$$\mathbf{Q} = \alpha \mathbf{a}^* + \beta \mathbf{b}^* + \gamma \mathbf{c}^*, \quad (1.10.1.3)$$

where at least one of  $\alpha$ ,  $\beta$  or  $\gamma$  is irrational. A simple example is the function  $\mathbf{f}_j(x) = \mathbf{A}_j \cos(2\pi x + \varphi_j)$ , where  $\mathbf{A}_j$  is the *polarization vector* and  $\varphi_j$  is the phase of the modulation. The diffraction pattern of the structure (1.10.1.2) shows spots at positions

$$\mathbf{H} = h_1 \mathbf{a}^* + h_2 \mathbf{b}^* + h_3 \mathbf{c}^* + h_4 \mathbf{Q}. \quad (1.10.1.4)$$

Therefore, the rank is four and  $\mathbf{a}_4^* = \mathbf{Q}$ . In a more general situation, the components of the atom positions in the IC phase are given by

$$\mathbf{n}^\alpha + \mathbf{r}_j^\alpha + \sum_m \mathbf{A}_j^\alpha(\mathbf{Q}_m) \cos(2\pi \mathbf{Q}_m \cdot \mathbf{n} + \varphi_{j\alpha}), \quad \alpha = x, y, z. \quad (1.10.1.5)$$

Here the vectors  $\mathbf{Q}_m$  belong to the Fourier module of the structure. Then there are vectors  $\mathbf{Q}_j$  such that any spot in the diffraction pattern can be written as

$$\mathbf{H} = \sum_{i=1}^3 h_i \mathbf{a}_i^* + \sum_{j=1}^d h_{3+j} \mathbf{Q}_j \quad (1.10.1.6)$$

and the rank is  $3 + d$ . The peaks corresponding to the basic structure [the combinations of the three reciprocal-lattice vectors  $\mathbf{a}_i^*$  ( $i = 1, 2, 3$ )] are called the *main reflections*, the other peaks are



## 1.11. Tensorial properties of local crystal susceptibilities

BY V. E. DMITRIENKO, A. KIRFEL AND E. N. OVCHINNIKOVA

### 1.11.1. Introduction

The tensorial characteristics of macroscopic physical properties (as described in Chapters 1.3, 1.4 and 1.6–1.8 of this volume) are determined by the crystal point group, whereas the symmetry of local crystal properties, such as atomic displacement parameters (Chapter 1.9) or electric field gradient tensors (Section 2.2.15) are regulated by the crystal space group. In the present chapter, we consider further examples of the impact of symmetry on local physical properties, particularly both symmetry and physical phenomena that allow and restrict forbidden reflections excited at radiation energies close to X-ray absorption edges of atoms, and reflections caused by magnetic scattering.

We begin with the X-ray dielectric susceptibility, which expresses the response of crystalline matter to an incident X-ray wave characterized by its energy (frequency), polarization and wavevector. The response is a polarization of the medium, finally resulting in a scattered wave with properties generally different from the initial ones. Thus, the dielectric susceptibility plays the role of a scattering amplitude, which relates the scattered wave to the incident wave. This is the basis of the different approaches to X-ray diffraction theories presented in Chapters 1.2 and 5.1 of *International Tables for Crystallography Volume B* (2008). Here, we consider only elastic scattering, *i.e.* the energies of the incident and scattered waves are identical, and the X-ray susceptibility is assumed to comply with the periodicity of the crystalline matter.

It is important that the dielectric susceptibility is (i) a local crystal property and (ii) a tensor physical property, because it relates the polarization vectors of the incident and scattered radiation. Consequently, the symmetry of the tensor is determined by the symmetry of the crystal space group, rather than by that of the point group as in conventional optics. In the vast majority of X-ray applications, this tensor can reasonably be assumed to be given by the product of the unit tensor and a scalar susceptibility, which is proportional to the electron density plus exclusively energy-dependent dispersion corrections as considered in Section 4.2.6 of *International Tables for Crystallography Volume C* (2004). As a result of atomic wavefunction distortions caused by neighbouring atoms, these scalar dispersion corrections can also become anisotropic tensors, namely in the close vicinity (usually less than about 50 eV) of absorption edges of elements. For heavy elements, the anisotropy of the tensor atomic factor can exceed  $20 e \text{ atom}^{-1}$ . Appropriate references to detailed descriptions of the phenomenon can be found in Brouder (1990), Materlik *et al.* (1994) and in Section 4.2.6 of Volume C (2004).

However, even if the anisotropy of the atomic factor is small, it can be crucial for some effects, for instance the excitation of so-called ‘forbidden’ reflections, which vanish in absence of anisotropy. Indeed, the crystal symmetry imposes strong restrictions on the indices of possible (‘allowed’) reflections. The systematic reflection conditions for the different space groups and for special atomic sites in the unit cell are listed in *International Tables for Crystallography Volume A* (Hahn, 2005). The resulting extinctions are due to (i) the translation symmetry of the non-

primitive Bravais lattices, (ii) the symmetry elements of the space group (glide planes and/or screw axes) and (iii) special sites. The first kind cannot be violated. The other extinctions are obtained if the atomic scattering factor (as the Fourier transform of an independent atom/ion with spherically symmetric electron-density distribution) is an element-specific scalar that depends only on the scattering-vector length and the dispersion corrections. Then the intensities of extinct reflections generally vanish. These reflections are ‘forbidden’, but for different physical reasons not all of their intensities are necessarily strictly zero. Such reflections can appear owing to an asphericity of (i) an atomic electron-density distribution caused by chemical bonding and/or (ii) atomic vibrations (Dawson, 1975) if the atom in question occupies a special site.

In contrast, an anisotropy of the atomic factor affects all reflections and can therefore violate general extinction rules related to glide planes and/or screw axes, *i.e.* symmetry elements with translation components, in nonsymmorphic space groups. Even a very small X-ray anisotropy can be quantitatively studied with this type of forbidden reflections, and yield information about electronic states of crystals or partial structures of resonant scatterers. This was first recognized by Templeton & Templeton (1980), and a detailed theory was developed only a few years later (Dmitrienko, 1983, 1984). The excitation of forbidden reflections caused by anisotropic anomalous scattering was first observed in an NaBrO<sub>3</sub> crystal (Templeton & Templeton, 1985, 1986) and then studied for Cu<sub>2</sub>O (Eichhorn & Kirfel, 1988), TiO<sub>2</sub> and MnF<sub>2</sub> (Kirfel & Petcov, 1991), and for many other compounds with different crystal symmetries. Within the dipole approximation, a systematic compilation of ‘forbidden’ reflection properties for all relevant space groups up to tetragonal symmetry and an application to partial-structure analysis followed (Kirfel *et al.*, 1991; Kirfel & Petcov, 1992; Kirfel & Morgenroth, 1993; Morgenroth *et al.*, 1994). Today, there are numerous surveys devoted to this well developed subject, and further details, applications and references can be found therein (Belyakov & Dmitrienko, 1989; Carra & Thole, 1994; Hodeau *et al.*, 2001; Lovesey *et al.*, 2005; Dmitrienko *et al.*, 2005; Altarelli, 2006; Collins *et al.*, 2007; Collins & Bombardi, 2010; Finkelstein & Dmitrienko, 2012). Forbidden reflections of the last type have also been observed (well before corresponding X-ray studies) in diffraction of Mössbauer radiation (Belyakov & Aivazyan, 1969; Belyakov, 1975; Champeney, 1979) and, at optical wavelengths, in the blue phases of chiral liquid crystals (Belyakov & Dmitrienko, 1985; Wright & Mermin, 1989; Seideman, 1990; Crooker, 2001). Similar phenomena have also been reported to exist in chiral smectic liquid crystals (Gleeson & Hirst, 2006; Barois *et al.*, 2012) and, considering neutron diffraction, in crystals with local anisotropy of the magnetic susceptibility (Gukasov & Brown, 2010). All these latter findings are, however, beyond the scope of this chapter.

X-ray polarization phenomena similar to those in visible optics and spectroscopy (birefringence, linear and circular dichroism, the Faraday rotation) have been discussed since the beginning of the 20th century (Hart & Rodrigues, 1981; Templeton & Templeton, 1980, 1982). Experimental studies and applications

## 1.11. TENSORIAL PROPERTIES OF LOCAL CRYSTAL SUSCEPTIBILITIES

### 1.11.5. Non-resonant magnetic scattering

Far from resonance ( $\hbar\omega \gg E_c - E_a$ ), the non-resonant parts of the scattering factor,  $f_0$  and  $f_{ij}^{\text{mag}}$ , described by the first two terms in (1.11.4.3) are the most important. In the classical approximation (Brunel & de Bergevin, 1981), there are four physical mechanisms (electric or magnetic, dipolar or quadrupolar) describing the interaction of an electron and its magnetic moment with an electromagnetic wave, causing the re-emission of radiation. The non-resonant magnetic term  $f^{\text{magn}}$  is small compared to the charge (Thomson) scattering owing (a) to small numbers of unpaired (magnetic) electrons and (b) to the factor  $\hbar\omega/mc^2$  of about 0.02 for a typical X-ray energy  $\hbar\omega = 10$  keV. This is the reason why it is so difficult to observe non-resonant magnetic scattering with conventional X-ray sources (de Bergevin & Brunel, 1972, 1981; Brunel & de Bergevin, 1981), in contrast to the nowadays normal use of synchrotron radiation.

Non-resonant magnetic scattering yields polarization properties quite different from those obtained from charge scattering. Moreover, it can be divided into two parts, which are associated with the spin and orbital moments. In contrast to the case of neutron magnetic scattering, the polarization properties of these two parts are different, as described by the tensors (Blume, 1994)

$$A_{ijk} = -2(1 - \mathbf{k} \cdot \mathbf{k}'/k^2)\epsilon_{ijk}, \quad (1.11.5.1)$$

$$B_{ijk} = \epsilon_{ijk} - [\epsilon_{ik}k'_j k'_j - \epsilon_{jk}k_i k_i + \frac{1}{2}\epsilon_{ijl}(k'_l k_k + k_l k'_k) - \frac{1}{2}[\mathbf{k} \times \mathbf{k}']_i \delta_{jk} - \frac{1}{2}[\mathbf{k} \times \mathbf{k}']_j \delta_{ik}]/k^2, \quad (1.11.5.2)$$

where  $\epsilon_{ijk}$  is a completely antisymmetric unit tensor (the Levi-Civita symbol).

Being convoluted with polarization vectors (Blume, 1985; Lovesey & Collins, 1996; Paolasini, 2012), the non-resonant magnetic term can be rewritten as

$$f_{\text{nonres}}^{\text{magn}}(\mathbf{G}) = -i \frac{\hbar\omega}{mc^2} \langle a | \sum_p (\mathbf{A} \cdot [\mathbf{G} \times \mathbf{P}_p]/\hbar k^2 + \mathbf{B} \cdot \mathbf{s}_p) \exp(i\mathbf{G} \cdot \mathbf{r}_p) | a \rangle, \quad (1.11.5.3)$$

with vectors  $\mathbf{A}$  and  $\mathbf{B}$  given by

$$\mathbf{A} = [\mathbf{e}^* \times \mathbf{e}], \quad (1.11.5.4)$$

$$\mathbf{B} = [\mathbf{e}^* \times \mathbf{e}] - \{[\mathbf{k} \times \mathbf{e}](\mathbf{k} \cdot \mathbf{e}^*) - [\mathbf{k}' \times \mathbf{e}^*](\mathbf{k}' \cdot \mathbf{e}) + [\mathbf{k}' \times \mathbf{e}^*] \times [\mathbf{k} \times \mathbf{e}]/k^2\}. \quad (1.11.5.5)$$

According to (1.11.5.4) and (1.11.5.5), the polarization dependences of the spin and orbit contributions to the atomic scattering factor are significantly different. Consequently, the two contributions can be separated by analysing the polarization of the scattered radiation with the help of an analyser crystal (Gibbs *et al.*, 1988). Usually the incident (synchrotron) radiation is  $\sigma$ -polarized, *i.e.* the polarization vector is perpendicular to the scattering plane. If due to the orientation of the analysing crystal only the  $\sigma$ -polarized part of the scattered radiation is recorded, we can see from (1.11.5.4) that the orbital contribution to the scattering atomic factor vanishes, whereas it differs from zero considering the  $\sigma \rightarrow \pi$  scattering channel.

### 1.11.6. Resonant atomic factors: multipole expansion

Strong enhancement of resonant scattering occurs when the energy of the incident radiation gets close to the energy of an

Table 1.11.6.1. Coefficients  $\gamma$  corresponding to various kinds of tensor symmetry with respect to space inversion  $\bar{1}$ , rotations  $R$ , and time reversal  $1'$

Tensor type	Example	Transformation type			
		$R$	$\bar{1}R$	$1'R$	$\bar{1}'R$
Even	Strain	1	1	1	1
Electric	Electric field	1	-1	1	-1
Magnetic	Magnetic field	1	1	-1	-1
Magnetolectric	Toroidal moment	1	-1	-1	1

electron transition from an inner shell to an empty state (be it localized or not) above the Fermi level. There are two widely used approaches for calculating resonant atomic amplitudes. One uses Cartesian, the other spherical (polar) coordinates, and both have their own advantages and disadvantages. Supposing in (1.11.4.3)

$$\exp(i\mathbf{k} \cdot \mathbf{r}_p) \approx 1 + i\mathbf{k} \cdot \mathbf{r}_p + \frac{1}{2}(i\mathbf{k} \cdot \mathbf{r}_p)^2 + \dots \quad (1.11.6.1)$$

and using the expression for the velocity matrix element  $v_{ac}$  (Berestetskii *et al.*, 1982)  $v_{ac} = i\omega_{ac}r_{ac}$ , it is possible to present the resonant part of the atomic factor (1.11.4.3) as

$$f_{jk}^{\text{res}} = \sum_c p_a \frac{m\omega_{ca}^3}{\omega} \left\{ \frac{\langle a|R_j|c\rangle\langle c|R_k|a\rangle}{E_a - E_c + \hbar\omega - i\Gamma/2} + \frac{i}{2} \left[ \frac{\langle a|R_j|c\rangle\langle c|R_k R_l k_l|a\rangle}{E_a - E_c + \hbar\omega - i\Gamma/2} - \frac{\langle a|R_j R_l k_l|c\rangle\langle c|R_k|a\rangle}{E_a - E_c + \hbar\omega - i\Gamma/2} \right] + \frac{1}{4} \frac{\langle a|R_j R_l k_l|c\rangle\langle c|R_k R_m k_m|a\rangle}{E_a - E_c + \hbar\omega - i\Gamma/2} \right\} \quad (1.11.6.2)$$

$$= D_{jk} + \frac{i}{2} I_{jkl} k_l - \frac{i}{2} I_{kjl} k'_l + \frac{1}{4} Q_{jklm} k_m k'_l, \quad (1.11.6.3)$$

where  $\hbar\omega_{ca} = E_c - E_a$ ,  $D_{jk}$  is a dimensionless tensor corresponding to the dipole-dipole ( $E1E1$ ) contribution,  $I_{jkl}$  is the dipole-quadrupole ( $E1E2$ ) contribution and  $Q_{jklm}$  is the quadrupole-quadrupole ( $E2E2$ ) term. All the tensors are complex and depend on the energy and the local properties of the medium. The expansion (1.11.6.1) over the wavevectors is possible near X-ray absorption edges because the products  $\mathbf{k} \cdot \mathbf{r}_p$  are small for the typical sizes of the inner shells involved. In resonant X-ray absorption and scattering, the contribution of the magnetic multipole  $ML$  transitions is usually much less than that of the electric multipole  $EL$  transitions. Nevertheless, the scattering amplitude corresponding to  $E1M1$  events has also been considered (Collins *et al.*, 2007). The tensors  $I_{jkl}$  and  $Q_{jklm}$  describe the spatial dispersion effects similar to those in visible optics.

#### 1.11.6.1. Tensor atomic factors: internal symmetry

Different types of tensors transform under the action of the extended orthogonal group (Sirotn & Shaskolskaya, 1982) as

$$A_{i_1 \dots i_n} = \gamma r_{i_1 k_1} \dots r_{i_n k_n} A_{k_1 \dots k_n}, \quad (1.11.6.4)$$

where the coefficients  $\gamma = \pm 1$  depend on the kind of tensor (see Table 1.11.6.1) and  $r_{i_1 k_1}$  are coefficients describing proper rotations.

Various parts of the resonant scattering factor (1.11.6.3) possess different kinds of symmetry with respect to: (1) space inversion  $\bar{1}$  or parity, (2) rotations  $R$  and (3) time reversal  $1'$ . Both dipole-dipole and quadrupole-quadrupole terms are parity-even, whereas the dipole-quadrupole term is parity-odd. Thus,

## 2. SYMMETRY ASPECTS OF EXCITATIONS

$$\mathbf{e}(\mathbf{q}, j) = \begin{pmatrix} \mathbf{e}_1(\mathbf{q}, j) \\ \vdots \\ \mathbf{e}_N(\mathbf{q}, j) \end{pmatrix} = \begin{pmatrix} e_1^x(\mathbf{q}, j) \\ e_1^y(\mathbf{q}, j) \\ e_1^z(\mathbf{q}, j) \\ \vdots \\ e_N^x(\mathbf{q}, j) \\ e_N^y(\mathbf{q}, j) \\ e_N^z(\mathbf{q}, j) \end{pmatrix} \quad (2.1.2.18)$$

and simultaneously the  $3 \times 3$  matrices  $\mathbf{F}_{\kappa\kappa'}(\mathbf{q})$  to a  $3N \times 3N$  matrix  $\mathbf{F}(\mathbf{q})$

$$\mathbf{F}(\mathbf{q}) = \begin{pmatrix} F_{11}^{xx} & F_{11}^{xy} & F_{11}^{xz} & & & & F_{1N}^{xx} & F_{1N}^{xy} & F_{1N}^{xz} \\ F_{11}^{yx} & F_{11}^{yy} & F_{11}^{yz} & & & & F_{1N}^{yx} & F_{1N}^{yy} & F_{1N}^{yz} \\ F_{11}^{zx} & F_{11}^{zy} & F_{11}^{zz} & & & & F_{1N}^{zx} & F_{1N}^{zy} & F_{1N}^{zz} \\ & & & F_{\kappa\kappa'}^{xx} & F_{\kappa\kappa'}^{xy} & F_{\kappa\kappa'}^{xz} & & & \\ \vdots & & & F_{\kappa\kappa'}^{yx} & F_{\kappa\kappa'}^{yy} & F_{\kappa\kappa'}^{yz} & & & \\ & & & F_{\kappa\kappa'}^{zx} & F_{\kappa\kappa'}^{zy} & F_{\kappa\kappa'}^{zz} & & & \\ & & & & & & & & \\ F_{N1}^{xx} & F_{N1}^{xy} & F_{N1}^{xz} & & & & F_{NN}^{xx} & F_{NN}^{xy} & F_{NN}^{xz} \\ F_{N1}^{yx} & F_{N1}^{yy} & F_{N1}^{yz} & & & & F_{NN}^{yx} & F_{NN}^{yy} & F_{NN}^{yz} \\ F_{N1}^{zx} & F_{N1}^{zy} & F_{N1}^{zz} & & & & F_{NN}^{zx} & F_{NN}^{zy} & F_{NN}^{zz} \end{pmatrix}, \quad (2.1.2.19)$$

equation (2.1.2.17) can be written in matrix notation and takes the simple form

$$\omega_{\mathbf{q},j}^2 \mathbf{e}(\mathbf{q}, j) = [\mathbf{M}\mathbf{F}(\mathbf{q})\mathbf{M}] \mathbf{e}(\mathbf{q}, j) = \mathbf{D}(\mathbf{q}) \mathbf{e}(\mathbf{q}, j), \quad (2.1.2.20)$$

where the diagonal matrix

$$\mathbf{M} = \begin{pmatrix} \frac{1}{\sqrt{m_1}} & 0 & 0 & & & \\ 0 & \frac{1}{\sqrt{m_1}} & 0 & & & \\ 0 & 0 & \frac{1}{\sqrt{m_1}} & & & \\ \vdots & & & \ddots & & \\ & & & & \frac{1}{\sqrt{m_N}} & 0 & 0 \\ & & & & 0 & \frac{1}{\sqrt{m_N}} & 0 \\ & & & & 0 & 0 & \frac{1}{\sqrt{m_N}} \end{pmatrix} \quad (2.1.2.21)$$

contains the masses of all atoms. The  $3N \times 3N$  matrix

$$\mathbf{D}(\mathbf{q}) = \mathbf{M}\mathbf{F}(\mathbf{q})\mathbf{M} \quad (2.1.2.22)$$

is called the *dynamical matrix*. It contains all the information about the dynamical behaviour of the crystal and can be calculated on the basis of specific models for interatomic interactions. In analogy to the  $3 \times 3$  matrices  $\mathbf{F}_{\kappa\kappa'}(\mathbf{q})$ , we introduce the submatrices of the dynamical matrix:

$$\mathbf{D}_{\kappa\kappa'}(\mathbf{q}) = \frac{1}{\sqrt{m_\kappa m_{\kappa'}}} \mathbf{F}_{\kappa\kappa'}(\mathbf{q}). \quad (2.1.2.22a)$$

Owing to the symmetry of the force-constant matrix,

$$V_{\alpha\beta}(\kappa l, \kappa' l') = V_{\beta\alpha}(\kappa' l', \kappa l), \quad (2.1.2.23)$$

the dynamical matrix is Hermitian:<sup>1</sup>

$$\mathbf{D}^T(\mathbf{q}) = \mathbf{D}^*(\mathbf{q}) = \mathbf{D}(-\mathbf{q}) \quad (2.1.2.24)$$

or more specifically

$$D_{\kappa\kappa'}^{\alpha\beta}(\mathbf{q}) = D_{\kappa'\kappa}^{\beta\alpha*}(\mathbf{q}) = D_{\kappa'\kappa}^{\beta\alpha}(-\mathbf{q}). \quad (2.1.2.24a)$$

Obviously, the squares of the vibrational frequency  $\omega_{\mathbf{q},j}$  and the polarization vectors  $\mathbf{e}(\mathbf{q}, j)$  are eigenvalues and corresponding eigenvectors of the dynamical matrix. As a direct consequence of

<sup>1</sup>The superscripts  $T$  and  $*$  are used to denote the transposed and the complex conjugate matrix, respectively.

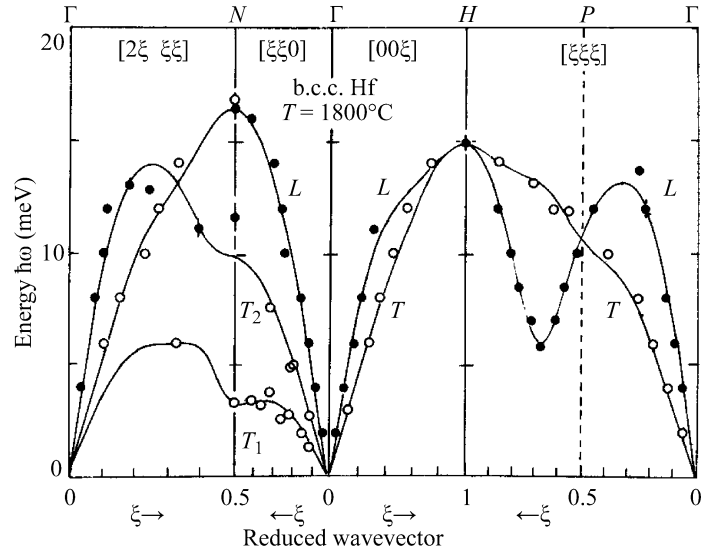


Fig. 2.1.2.3. Phonon dispersion of b.c.c. hafnium for wavevectors along the main symmetry directions of the cubic structure. The symbols represent experimental data obtained by inelastic neutron scattering and the full lines are the results of the model. From Trampenau *et al.* (1991). Copyright (1991) by the American Physical Society.

equation (2.1.2.20), the eigenvalues  $\omega_{\mathbf{q},j}^2$  are real quantities and the following relations hold:

$$\omega_{\mathbf{q},j}^2 = \omega_{-\mathbf{q},j}^2, \quad (2.1.2.25)$$

$$\mathbf{e}^*(\mathbf{q}, j) = \mathbf{e}(-\mathbf{q}, j). \quad (2.1.2.26)$$

Moreover, the eigenvectors are mutually orthogonal and can be chosen to be normalized.

### 2.1.2.4. Eigenvalues and phonon dispersion, acoustic modes

The wavevector dependence of the vibrational frequencies is called *phonon dispersion*. For each wavevector  $\mathbf{q}$  there are  $3N$  fundamental frequencies yielding  $3N$  phonon *branches* when  $\omega_{\mathbf{q},j}$  is plotted *versus*  $\mathbf{q}$ . In most cases, the phonon dispersion is displayed for wavevectors along high-symmetry directions. These dispersion curves are, however, only special projections of the dispersion hypersurface in the four-dimensional  $\mathbf{q}$ - $\omega$  space. As a simple example, the phonon dispersion of b.c.c. hafnium is displayed in Fig. 2.1.2.3. The wavevectors are restricted to the first Brillouin zone (see Section 2.1.3.1) and the phonon dispersion for different directions of the wavevector are combined in one single diagram making use of the fact that different high-symmetry directions meet at the Brillouin-zone boundary. Note that in Fig. 2.1.2.3, the moduli of the wavevectors are scaled by the Brillouin-zone boundary values and represented by the reduced coordinates  $\xi$ . Owing to the simple b.c.c. structure of hafnium with one atom per primitive cell, there are only three phonon branches. Moreover, for all wavevectors along the directions  $[00\xi]$  and  $[\xi\xi\xi]$ , two exhibit the same frequencies – they are said to be *degenerate*. Hence in the corresponding parts of Fig. 2.1.2.3 only two branches can be distinguished.

Whereas in this simple example the different branches can be separated quite easily, this is no longer true for more complicated crystal structures. For illustration, the phonon dispersion of the high- $T_c$  superconductor  $\text{Nd}_2\text{CuO}_4$  is shown in Fig. 2.1.2.4 for the main symmetry directions of the tetragonal structure (space group  $I4/mmm$ , seven atoms per primitive cell). Note that in many publications on lattice dynamics the frequency  $\nu = \omega/2\pi$  is used rather than the angular frequency  $\omega$ .

The 21 phonon branches of  $\text{Nd}_2\text{CuO}_4$  with their more complicated dispersion reflect the details of the interatomic interactions between all atoms of the structure. The phonon frequencies  $\nu$  cover a range from 0 to 18 THz. In crystals with

## 2.2.5. The free-electron (Sommerfeld) model

The free-electron model corresponds to the special case of taking a constant potential in the Schrödinger equation (2.2.4.1). The physical picture relies on the assumption that the (metallic) valence electrons can move freely in the field of the positively charged nuclei and the tightly bound core electrons. Each valence electron moves in a potential which is nearly constant due to the screening of the remaining valence electrons. This situation can be idealized by assuming the potential to be constant [ $V(\mathbf{r}) = 0$ ]. This simple picture represents a crude model for simple metals but has its importance mainly because the corresponding equation can be solved analytically. By rewriting equation (2.2.4.1), we have

$$\nabla^2 \psi_{\mathbf{k}}(\mathbf{r}) = -\frac{2mE}{\hbar^2} \psi_{\mathbf{k}}(\mathbf{r}) = -|\mathbf{k}|^2 \psi_{\mathbf{k}}(\mathbf{r}), \quad (2.2.5.1)$$

where in the last step the constants are abbreviated (for later convenience) by  $|\mathbf{k}|^2$ . The solutions of this equation are plane waves (PWs)

$$\psi_{\mathbf{k}}(\mathbf{r}) = C \exp(i\mathbf{k} \cdot \mathbf{r}), \quad (2.2.5.2)$$

where  $C$  is a normalization constant which is defined from the integral over one unit cell with volume  $\Omega$ . The PWs satisfy the Bloch condition and can be written (using the bra-ket notation) as

$$|\mathbf{k}\rangle = \psi_{\mathbf{k}}(\mathbf{r}) = \Omega^{1/2} \exp(i\mathbf{k} \cdot \mathbf{r}). \quad (2.2.5.3)$$

From (2.2.5.1) we see that the corresponding energy (labelled by  $\mathbf{k}$ ) is given by

$$E_{\mathbf{k}} = \frac{\hbar^2}{2m} |\mathbf{k}|^2. \quad (2.2.5.4)$$

In this context it is useful to consider the momentum of the electron, which classically is the vector  $\mathbf{p} = m\mathbf{v}$ , where  $m$  and  $\mathbf{v}$  are the mass and velocity, respectively. In quantum mechanics we must replace  $\mathbf{p}$  by the corresponding operator  $\mathbb{P}$ .

$$\mathbb{P}|\mathbf{k}\rangle = \frac{\hbar}{i} \frac{\partial}{\partial \mathbf{r}} |\mathbf{k}\rangle = \frac{\hbar}{i} i\mathbf{k} |\mathbf{k}\rangle = \hbar\mathbf{k} |\mathbf{k}\rangle. \quad (2.2.5.5)$$

Thus a PW is an eigenfunction of the momentum operator with eigenvalue  $\hbar\mathbf{k}$ . Therefore the  $\mathbf{k}$  vector is also called the *momentum* vector. Note that this is strictly true for a vanishing potential but is otherwise only approximately true (referred to as *pseudomomentum*).

Another feature of a PW is that its phase is constant in a plane perpendicular to the vector  $\mathbf{k}$  (see Fig. 2.2.5.1). For this purpose, consider a periodic function in space and time,

$$\varphi_{\mathbf{k}}(\mathbf{r}, t) = \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)], \quad (2.2.5.6)$$

which has a constant phase factor  $\exp(i\omega t)$  within such a plane. We can characterize the spatial part by  $\mathbf{r}$  within this plane. Taking the nearest parallel plane (with vector  $\mathbf{r}'$ ) for which the same phase factors occur again but at a distance  $\lambda$  away (with the unit vector  $\mathbf{e}$  normal to the plane),

$$\mathbf{r}' = \mathbf{r} + \lambda \mathbf{e} = \mathbf{r} + \lambda \frac{\mathbf{k}}{|\mathbf{k}|}, \quad (2.2.5.7)$$

then  $\mathbf{k} \cdot \mathbf{r}'$  must differ from  $\mathbf{k} \cdot \mathbf{r}$  by  $2\pi$ . This is easily obtained from (2.2.5.7) by multiplication with  $\mathbf{k}$  leading to

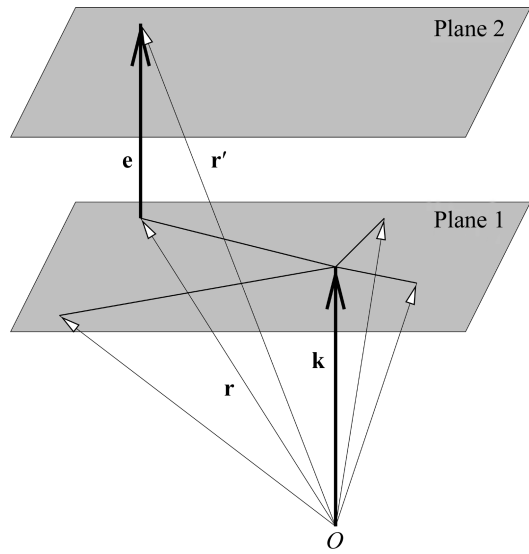


Fig. 2.2.5.1. Plane waves. The wavevector  $\mathbf{k}$  and the unit vector  $\mathbf{e}$  are normal to the two planes and the vectors  $\mathbf{r}$  in plane 1 and  $\mathbf{r}'$  in plane 2.

$$\mathbf{k} \cdot \mathbf{r}' = \mathbf{k} \cdot \mathbf{r} + \lambda \frac{|\mathbf{k}|^2}{|\mathbf{k}|} = \mathbf{k} \cdot \mathbf{r} + \lambda |\mathbf{k}| \quad (2.2.5.8)$$

$$\mathbf{k} \cdot \mathbf{r}' - \mathbf{k} \cdot \mathbf{r} = \lambda |\mathbf{k}| = 2\pi \quad (2.2.5.9)$$

$$\lambda = \frac{2\pi}{|\mathbf{k}|} \text{ or } |\mathbf{k}| = \frac{2\pi}{\lambda}. \quad (2.2.5.10)$$

Consequently  $\lambda$  is the wavelength and thus the  $\mathbf{k}$  vector is called the *wavevector* or *propagation vector*.

## 2.2.6. Space-group symmetry

## 2.2.6.1. Representations and bases of the space group

The effect of a space-group operation  $\{p|\mathbf{w}\}$  on a Bloch function, labelled by  $\mathbf{k}$ , is to transform it into a Bloch function that corresponds to a vector  $p\mathbf{k}$ ,

$$\{p|\mathbf{w}\} \psi_{\mathbf{k}} = \psi_{p\mathbf{k}}, \quad (2.2.6.1)$$

which can be proven by using the multiplication rule of Seitz operators (2.2.3.12) and the definition of a Bloch state (2.2.4.17).

A special case is the inversion operator, which leads to

$$\{i|\mathbf{E}\} \psi_{\mathbf{k}} = \psi_{-\mathbf{k}}. \quad (2.2.6.2)$$

The Bloch functions  $\psi_{\mathbf{k}}$  and  $\psi_{p\mathbf{k}}$ , where  $p$  is any operation of the point group  $P$ , belong to the same basis for a representation of the space group  $G$ .

$$\langle \psi_{\mathbf{k}} | = \langle \psi_{p\mathbf{k}} | \text{ for all } p \in P \text{ for all } p\mathbf{k} \in \text{BZ}. \quad (2.2.6.3)$$

The same  $p\mathbf{k}$  cannot appear in two different bases, thus the two bases  $\psi_{\mathbf{k}}$  and  $\psi_{\mathbf{k}'}$  are either identical or have no  $\mathbf{k}$  in common.

Irreducible representations of  $T$  are labelled by the  $N$  distinct  $\mathbf{k}$  vectors in the BZ, which separate in disjoint bases of  $G$  (with no  $\mathbf{k}$  vector in common). If a  $\mathbf{k}$  vector falls on the BZ edge, application of the point-group operation  $p$  can lead to an equivalent  $\mathbf{k}'$  vector that differs from the original by  $\mathbf{K}$  (a vector of the reciprocal lattice). The set of all mutually inequivalent  $\mathbf{k}$  vectors of  $p\mathbf{k}$  ( $p \in P$ ) define the *star of the  $\mathbf{k}$  vector* ( $S_{\mathbf{k}}$ ) (see also Section 1.2.3.3 of the present volume).

The set of all operations that leave a  $\mathbf{k}$  vector invariant (or transform it into an equivalent  $\mathbf{k} + \mathbf{K}$ ) forms the *group*  $G_{\mathbf{k}}$  of the  $\mathbf{k}$  vector. Application of  $q$ , an element of  $G_{\mathbf{k}}$ , to a Bloch function (Section 2.2.8) gives

$$q \psi_{\mathbf{k}}^j(\mathbf{r}) = \psi_{\mathbf{k}}^j(\mathbf{r}) \text{ for } q \in G_{\mathbf{k}}, \quad (2.2.6.4)$$

## 2. SYMMETRY ASPECTS OF EXCITATIONS

Table 2.2.13.1. Picking rules for the local coordinate axes and the corresponding LM combinations ( $\ell mp$ ) of non-cubic groups taken from Kurki-Suonio (1977)

Symmetry	Coordinate axes	$\ell, m, p$ of $y_{\ell mp}$	Crystal system
$1$ $\bar{1}$	Any Any	All ( $\ell, m, \pm$ ) ( $2\ell, m, \pm$ )	Triclinic
$2$ $m$ $2/m$	$2 \parallel z$ $m \perp z$ $2 \parallel z, m \perp z$	( $\ell, 2m, \pm$ ) ( $\ell, \ell - 2m, \pm$ ) ( $2\ell, 2m, \pm$ )	Monoclinic
$222$ $mm2$ $mmm$	$2 \parallel z, 2 \parallel y$ ( $2 \parallel x$ ) $2 \parallel z, m \perp y$ ( $2 \perp x$ ) $2 \perp z, m \perp y, 2 \perp x$	( $2\ell, 2m, +$ ), ( $2\ell + 1, 2m, -$ ) ( $\ell, 2m, +$ ) ( $2\ell, 2m, +$ )	Orthorhombic
$4$ $\bar{4}$ $4/m$ $422$ $4mm$ $\bar{4}2m$ $4mmm$	$4 \parallel z$ $-4 \parallel z$ $4 \parallel z, m \perp z$ $4 \parallel z, 2 \parallel y$ ( $2 \parallel x$ ) $4 \parallel z, m \perp y$ ( $2 \perp x$ ) $-4 \parallel z, 2 \parallel x$ ( $m = xy \rightarrow yx$ ) $4 \parallel z, m \perp z, m \perp x$	( $\ell, 4m, \pm$ ) ( $2\ell, 4m, \pm$ ), ( $2\ell + 1, 4m + 2, \pm$ ) ( $2\ell, 4m, \pm$ ) ( $2\ell, 4m, +$ ), ( $2\ell + 1, 4m, -$ ) ( $\ell, 4m, +$ ) ( $2\ell, 4m, +$ ), ( $2\ell + 1, 4m + 2, -$ ) ( $2\ell, 4m, +$ )	Tetragonal
$3$ $\bar{3}$ $32$ $3m$ $\bar{3}m$	$3 \parallel z$ $-3 \parallel z$ $3 \parallel z, 2 \parallel y$ $3 \parallel z, m \perp y$ $-3 \parallel z, m \perp y$	( $\ell, 3m, \pm$ ) ( $2\ell, 3m, \pm$ ) ( $2\ell, 3m, +$ ), ( $2\ell + 1, 3m, -$ ) ( $\ell, 3m, +$ ) ( $2\ell, 3m, +$ )	Rhombohedral
$6$ $\bar{6}$ $6/m$ $622$ $6mm$ $\bar{6}2m$ $6mmm$	$6 \parallel z$ $-6 \parallel z$ $6 \parallel z, m \perp z$ $6 \parallel z, 2 \parallel y$ ( $2 \parallel x$ ) $6 \parallel z, m \parallel y$ ( $m \perp x$ ) $-6 \parallel z, m \perp y$ ( $2 \parallel x$ ) $6 \parallel z, m \perp z, m \perp y$ ( $m \perp x$ )	( $\ell, 6m, \pm$ ) ( $2\ell, 6m, +$ ), ( $2\ell + 1, 6m + 3, \pm$ ) ( $2\ell, 6m, \pm$ ) ( $2\ell, 6m, +$ ), ( $2\ell + 1, 6m, -$ ) ( $\ell, 6m, +$ ) ( $2\ell, 6m, +$ ), ( $2\ell + 1, 6m + 3, +$ ) ( $2\ell, 6m, +$ )	Hexagonal

Therefore in the MTA one must make a compromise, whereas in full-potential calculations this problem practically disappears.

### 2.2.13. The local coordinate system

The partition of a crystal into atoms (or molecules) is ambiguous and thus the atomic contribution cannot be defined uniquely. However, whatever the definition, it must follow the relevant site symmetry for each atom. There are at least two reasons why one would want to use a *local coordinate system* at each atomic site: the concept of crystal harmonics and the interpretation of bonding features.

#### 2.2.13.1. Crystal harmonics

All spatial observables of the bound atom (*e.g.* the potential or the charge density) must have the crystal symmetry, *i.e.* the point-group symmetry around an atom. Therefore they must be representable as an expansion in terms of site-symmetrized spherical harmonics. Any point-symmetry operation transforms a spherical harmonic into another of the same  $\ell$ . We start with the usual complex spherical harmonics,

$$Y_{\ell m}(\vartheta, \varphi) = N_{\ell m} P_{\ell}^m(\cos \vartheta) \exp(im\varphi), \quad (2.2.13.1)$$

which satisfy Laplacian's differential equation. The  $P_{\ell}^m(\cos \vartheta)$  are the associated Legendre polynomials and the normalization  $N_{\ell m}$  is according to the convention of Condon & Shortley (1953). For the  $\varphi$ -dependent part one can use the real and imaginary part and thus use  $\cos(m\varphi)$  and  $\sin(m\varphi)$  instead of the  $\exp(im\varphi)$  functions,

Table 2.2.13.2. LM combinations of cubic groups as linear combinations of  $y_{\ell mp}$ 's (given in parentheses)

The linear-combination coefficients can be found in Kurki-Suonio (1977).

Symmetry	LM combinations
23	(0 0), (3 2-), (4 0, 4 4+), (6 0, 6 4+), (6 2+, 6 6+)
$m\bar{3}$	(0 0), (4 0, 4 4+), (6 0, 6 4+) (6 2+, 6 6+)
432	(0 0), (4 0, 4 4+), (6 0, 6 4+)
$\bar{4}3m$	(0 0), (3 2-), (4 0, 4 4+), (6 0, 6 4+),
$m\bar{3}m$	(0 0), (4 0, 4 4+), (6 0, 6 4+)

but we must introduce a parity  $p$  to distinguish the functions with the same  $|m|$ . For convenience we take real spherical harmonics, since physical observables are real. The even and odd polynomials are given by the combination of the complex spherical harmonics with the parity  $p$  either + or - by

$$y_{\ell mp} = \begin{cases} y_{\ell m+} = (1/\sqrt{2})(Y_{\ell m} + Y_{\ell \bar{m}}) & + \text{parity} \\ y_{\ell m-} = -(i/\sqrt{2})(Y_{\ell m} - Y_{\ell \bar{m}}) & - \text{parity} \end{cases}, m = 2n$$

$$y_{\ell mp} = \begin{cases} y_{\ell m+} = -(1/\sqrt{2})(Y_{\ell m} - Y_{\ell \bar{m}}) & + \text{parity} \\ y_{\ell m-} = (i/\sqrt{2})(Y_{\ell m} + Y_{\ell \bar{m}}) & - \text{parity} \end{cases}, m = 2n + 1. \quad (2.2.13.2)$$

The expansion of - for example - the charge density  $\rho(\mathbf{r})$  around an atomic site can be written using the LAPW method [see the analogous equation (2.2.12.5) for the potential] in the form

$$\rho(\mathbf{r}) = \sum_{LM} \rho_{LM}(\mathbf{r}) K_{LM}(\hat{\mathbf{r}}) \text{ inside an atomic sphere,} \quad (2.2.13.3)$$

where we use capital letters  $LM$  for the indices (i) to distinguish this expansion from that of the wavefunctions in which complex spherical harmonics are used [see (2.2.12.1)] and (ii) to include the parity  $p$  in the index  $M$  (which represents the combined index  $mp$ ). With these conventions,  $K_{LM}$  can be written as a linear combination of real spherical harmonics  $y_{\ell mp}$  which are symmetry-adapted to the site symmetry,

$$K_{LM}(\hat{\mathbf{r}}) = \begin{cases} y_{\ell mp} & \text{non-cubic} \\ \sum_j c_{Lj} y_{\ell j p} & \text{cubic} \end{cases} \quad (2.2.13.4)$$

*i.e.* they are either  $y_{\ell mp}$  [(2.2.13.2)] in the non-cubic cases (Table 2.2.13.1) or are well defined combinations of  $y_{\ell mp}$ 's in the five cubic cases (Table 2.2.13.2), where the coefficients  $c_{Lj}$  depend on the normalization of the spherical harmonics and can be found in Kurki-Suonio (1977).

According to Kurki-Suonio, the number of (non-vanishing)  $LM$  terms [*e.g.* in (2.2.13.3)] is minimized by choosing for each atom a local Cartesian coordinate system adapted to its site

## 2.3. Raman scattering

BY I. GREGORA

### 2.3.1. Introduction

The term Raman scattering, traditionally used for light scattering by molecular vibrations or optical lattice vibrations in crystals, is often applied in a general sense to a vast variety of phenomena of inelastic scattering of photons by various excitations in molecules, solids or liquids. In crystals these excitations may be collective (phonons, plasmons, polaritons, magnons) or single-particle (electrons, electron-hole pairs, vibrational and electronic excitation of impurities). Raman scattering provides an important tool for the study of the properties of these excitations. In the present chapter, we shall briefly review the general features of Raman scattering in perfect crystals on a phenomenological basis, paying special attention to the consequences of the crystal symmetry. Our focus will be mainly on Raman scattering by vibrational excitations of the crystal lattice – *phonons*. Nevertheless, most of the conclusions have general validity and may be (with possible minor modifications) transferred also to inelastic scattering by other excitations.

### 2.3.2. Inelastic light scattering in crystals – basic notions

Although quantum concepts must be used in any complete theory of inelastic scattering, basic insight into the problem may be obtained from a semiclassical treatment. In classical terms, the origin of inelastically scattered light in solids should be seen in the modulation of the dielectric susceptibility of a solid by elementary excitations. The exciting light polarizes the solid and the polarization induced *via* the modulated part of the susceptibility is re-radiated at differently shifted frequencies. Thus inelastic scattering of light by the temporal and spatial fluctuations of the dielectric susceptibility that are induced by elementary excitations provides information about the symmetry and wavevector-dependent frequencies of the excitations themselves as well as about their interaction with electromagnetic waves.

#### 2.3.2.1. Kinematics

Let us consider the incident electromagnetic radiation, the scattered electromagnetic radiation and the elementary excitation to be described by plane waves. The incident radiation is characterized by frequency  $\omega_I$ , wavevector  $\mathbf{k}_I$  and polarization vector  $\mathbf{e}_I$ . Likewise, the scattered radiation is characterized by  $\omega_S$ ,  $\mathbf{k}_S$  and  $\mathbf{e}_S$ :

$$\mathbf{E}_{I,S}(\mathbf{r}, t) = E_{I,S} \mathbf{e}_{I,S} \exp(i\mathbf{k}_{I,S} \cdot \mathbf{r} - \omega t). \quad (2.3.2.1)$$

The scattering process involves the annihilation of the incident photon, the emission or annihilation of one or more quanta of elementary excitations and the emission of a scattered photon. The scattering is characterised by a *scattering frequency*  $\omega$  (also termed the *Raman shift*) corresponding to the energy transfer  $\hbar\omega$  from the radiation field to the crystal, and by a *scattering wavevector*  $\mathbf{q}$  corresponding to the respective momentum transfer  $\hbar\mathbf{q}$ . Since the energy and momentum must be conserved in the scattering process, we have the conditions

$$\begin{aligned} \omega_I - \omega_S &= \omega, \\ \mathbf{k}_I - \mathbf{k}_S &= \mathbf{q}. \end{aligned} \quad (2.3.2.2)$$

Strictly speaking, the momentum conservation condition is valid only for sufficiently large, perfectly periodic crystals. It is further assumed that there is no significant absorption of the incident and

scattered light beams, so that the wavevectors may be considered real quantities.

Since the photon wavevectors ( $\mathbf{k}_I, \mathbf{k}_S$ ) and frequencies ( $\omega_I, \omega_S$ ) are related by the dispersion relation  $\omega = ck/n$ , where  $c$  is the speed of light in free space and  $n$  is the refractive index of the medium at the respective frequency, the energy and wavevector conservation conditions imply for the magnitude of the scattering wavevector  $q$

$$c^2 q^2 = n_I^2 \omega_I^2 + n_S^2 (\omega_I - \omega)^2 - 2n_I n_S \omega_I (\omega_I - \omega) \cos \varphi, \quad (2.3.2.3)$$

where  $\varphi$  is the *scattering angle* (the angle between  $\mathbf{k}_I$  and  $\mathbf{k}_S$ ). This relation defines in the  $(\omega, q)$  plane the region of wavevectors and frequencies accessible to the scattering. This relation is particularly important for scattering by excitations whose frequencies depend markedly on the scattering wavevector (*e.g.* acoustic phonons, polaritons *etc.*).

#### 2.3.2.2. Cross section

In the absence of any excitations, the incident field  $\mathbf{E}_I$  at frequency  $\omega_I$  induces in the crystal the polarization  $\mathbf{P}$ , related to the field by the *linear* dielectric susceptibility tensor  $\chi$  ( $\epsilon_0$  is the permittivity of free space):

$$\mathbf{P} = \epsilon_0 \chi(\omega_I) \mathbf{E}_I. \quad (2.3.2.4)$$

The linear susceptibility  $\chi(\omega_I)$  is understood to be independent of position, depending on the crystal characteristics and on the frequency of the radiation field only. In the realm of nonlinear optics, additional terms of higher order in the fields may be considered; they are expressed through the respective *nonlinear* susceptibilities.

The effect of the excitations is to modulate the wavefunctions and the energy levels of the medium, and can be represented macroscopically as an additional contribution to the linear susceptibility. Treating this modulation as a perturbation, the resulting contribution to the susceptibility tensor, the so-called *transition susceptibility*  $\delta\chi$  can be expressed as a Taylor expansion in terms of *normal coordinates*  $Q_j$  of the excitations:

$$\chi \rightarrow \chi + \delta\chi, \quad \text{where } \delta\chi = \sum_j \chi^{(j)} Q_j + \sum_{j,j'} \chi^{(j,j')} Q_j Q_{j'} + \dots \quad (2.3.2.5)$$

The tensorial coefficients  $\chi^{(j)}, \chi^{(j,j)}, \dots$  in this expansion are, in a sense, *higher-order susceptibilities* and are often referred to as *Raman tensors* (of the first, second and higher orders). They are obviously related to *susceptibility derivatives* with respect to the normal coordinates of the excitations. The time-dependent polarization induced by  $\delta\chi$  *via* time dependence of the normal coordinates can be regarded as the source of the inelastically scattered radiation.

The central quantity in the description of Raman scattering is the *spectral differential cross section*, defined as the relative rate of energy loss from the incident beam (frequency  $\omega_I$ , polarization  $\mathbf{e}_I$ ) as a result of its scattering (frequency  $\omega_S$ , polarization  $\mathbf{e}_S$ ) in volume  $V$  into a unit solid angle and unit frequency interval. The corresponding formula may be concisely written as (see *e.g.* Hayes & Loudon, 1978)

$$\frac{d^2\sigma}{d\Omega d\omega_S} = \frac{\omega_S^3 \omega_I V^2 n_S}{(4\pi)^2 c^4 n_I} \left| \mathbf{e}_I \delta\chi \mathbf{e}_S \right|_{\omega}^2. \quad (2.3.2.6)$$

## 2.4. BRILLOUIN SCATTERING

dissipation theorem in the classical limit for  $h\delta\nu \ll k_B T$  (Hayes & Loudon, 1978). The coupling coefficient  $M$  is given by

$$M = |e_m e'_n \kappa_{mi} \kappa_{nj} p'_{ijk\ell} \hat{u}_k \hat{Q}_\ell|^2. \quad (2.4.4.8)$$

In practice, the incident intensity is defined outside the scattering volume,  $I_{\text{out}}$ , and for normal incidence one can write

$$I_{\text{in}} = \frac{4n}{(n+1)^2} I_{\text{out}}. \quad (2.4.4.9a)$$

Similarly, the scattered power is observed outside as  $P_{\text{out}}$ , and

$$P_{\text{out}} = \frac{4n'}{(n'+1)^2} P_{\text{in}}, \quad (2.4.4.9b)$$

again for normal incidence. Finally, the approximative relation between the scattering solid angle  $\Omega_{\text{out}}$ , outside the sample, and the solid angle  $\Omega_{\text{in}}$ , in the sample, is

$$\Omega_{\text{out}} = (n')^2 \Omega_{\text{in}}. \quad (2.4.4.9c)$$

Substituting (2.4.4.9a,b,c) in (2.4.4.7), one obtains (Vacher & Boyer, 1972)

$$\frac{dP_{\text{out}}}{d\Omega_{\text{out}}} = \frac{8\pi^2 k_B T}{\lambda_0^4} \frac{n^4}{(n+1)^2} \frac{(n')^4}{(n'+1)^2} \beta V I_{\text{out}}, \quad (2.4.4.10)$$

where the coupling coefficient  $\beta$  is

$$\beta = \frac{1}{n^4 (n')^4} \frac{|e_m e'_n \kappa_{mi} \kappa_{nj} p'_{ijk\ell} \hat{u}_k \hat{Q}_\ell|^2}{C}. \quad (2.4.4.11)$$

In the cases of interest here, the tensor  $\kappa$  is diagonal,  $\kappa_{ij} = n_i^2 \delta_{ij}$  without summation on  $i$ , and (2.4.4.11) can be written in the simpler form

$$\beta = \frac{1}{n^4 (n')^4} \frac{|e_i n_i^2 p'_{ijk\ell} \hat{u}_k \hat{Q}_\ell e'_j n_j^2|^2}{C}. \quad (2.4.4.12)$$

### 2.4.5. Use of the tables

The tables in this chapter give information on modes and scattering geometries that are in most common use in the study of hypersound in single crystals. Just as in the case of X-rays, Brillouin scattering is not sensitive to the presence or absence of a centre of symmetry (Friedel, 1913). Hence, the results are the same for all crystalline classes belonging to the same centric group, also called Laue class. The correspondence between the point groups and the Laue classes analysed here is shown in Table 2.4.5.1. The monoclinic and triclinic cases, being too cumbersome, will not be treated here.

For tensor components  $c_{ijkl}$  and  $p_{ijk\ell}$ , the tables make use of the usual contracted notation for index pairs running from 1 to 6. However, as the tensor  $p'_{ijk\ell}$  is not symmetric upon interchange of  $(k, \ell)$ , it is necessary to distinguish the order  $(k, \ell)$  and  $(\ell, k)$ . This is accomplished with the following correspondence:

$$\begin{aligned} 1, 1 &\rightarrow 1 & 2, 2 &\rightarrow 2 & 3, 3 &\rightarrow 3 \\ 1, 2 &\rightarrow 6 & 2, 3 &\rightarrow 4 & 3, 1 &\rightarrow 5 \\ 2, 1 &\rightarrow \bar{6} & 3, 2 &\rightarrow \bar{4} & 1, 3 &\rightarrow \bar{5}. \end{aligned}$$

Geometries for longitudinal modes (LA) are listed in Tables 2.4.5.2 to 2.4.5.8. The first column gives the direction of the scattering vector  $\hat{\mathbf{Q}}$  that is parallel to the displacement  $\hat{\mathbf{u}}$ . The second column gives the elastic coefficient according to (2.4.2.6). In piezoelectric materials, effective elastic coefficients defined in (2.4.2.11) must be used in this column. The third column gives the direction of the light polarizations  $\hat{\mathbf{e}}$  and  $\hat{\mathbf{e}}'$ , and the last column

gives the corresponding coupling coefficient  $\beta$  [equation (2.5.5.11)]. In general, the strongest scattering intensity is obtained for polarized scattering ( $\hat{\mathbf{e}} = \hat{\mathbf{e}}'$ ), which is the only situation listed in the tables. In this case, the coupling to light ( $\beta$ ) is independent of the scattering angle  $\theta$ , and thus the tables apply to any  $\theta$  value.

Tables 2.4.5.9 to 2.4.5.15 list the geometries usually used for the observation of TA modes in backscattering ( $\theta = 180^\circ$ ). In this case,  $\hat{\mathbf{u}}$  is always perpendicular to  $\hat{\mathbf{Q}}$  (pure transverse modes), and  $\hat{\mathbf{e}}'$  is not necessarily parallel to  $\hat{\mathbf{e}}$ . Cases where pure TA modes with  $\hat{\mathbf{u}}$  in the plane perpendicular to  $\hat{\mathbf{Q}}$  are degenerate are indicated by the symbol  $D$  in the column for  $\hat{\mathbf{u}}$ . For the Pockels tensor components, the notation is  $p_{\alpha\beta}$  if the rotational term vanishes by symmetry, and it is  $p'_{\alpha\beta}$  otherwise.

Tables 2.4.5.16 to 2.4.5.22 list the common geometries used for the observation of TA modes in  $90^\circ$  scattering. In these tables, the polarization vector  $\hat{\mathbf{e}}$  is always perpendicular to the scattering plane and  $\hat{\mathbf{e}}'$  is always parallel to the incident wavevector of light  $\mathbf{q}$ . Owing to birefringence, the scattering vector  $\hat{\mathbf{Q}}$  does not exactly bisect  $\mathbf{q}$  and  $\mathbf{q}'$  [equation (2.4.4.4)]. The tables are written for strict  $90^\circ$  scattering,  $\mathbf{q} \cdot \mathbf{q}' = 0$ , and in the case of birefringence the values of  $\mathbf{q}^{(m)}$  to be used are listed separately in Table 2.4.5.23. The latter assumes that the birefringences are not large, so that the values of  $\mathbf{q}^{(m)}$  are given only to first order in the birefringence.

### 2.4.6. Techniques of Brillouin spectroscopy

Brillouin spectroscopy with visible laser light requires observing frequency shifts falling typically in the range  $\sim 1$  to  $\sim 100$  GHz, or  $\sim 0.03$  to  $\sim 3$   $\text{cm}^{-1}$ . To achieve this with good resolution one mostly employs interferometry. For experiments at very small angles (near forward scattering), photocorrelation spectroscopy can also be used. If the observed frequency shifts are  $\geq 1$   $\text{cm}^{-1}$ , rough measurements of spectra can sometimes be obtained with modern grating instruments. Recently, it has also become possible to perform Brillouin scattering using other excitations, in particular neutrons or X-rays. In these cases, the coupling does not occur *via* the Pockels effect, and the frequency shifts that are observed are much larger. The following discussion is restricted to optical interferometry.

The most common interferometer that has been used for this purpose is the single-pass planar Fabry–Perot (Born & Wolf, 1993). Upon illumination with monochromatic light, the frequency response of this instrument is given by the Airy function, which consists of a regular comb of maxima obtained as the optical path separating the mirrors is increased. Successive maxima are separated by  $\lambda/2$ . The ratio of the maxima separation to the width of a single peak is called the finesse  $F$ , which increases as the mirror reflectivity increases. The finesse is also limited by the planarity of the mirrors. A practical limit is  $F \sim 100$ . The resolving power of such an instrument is  $R = 2\ell/\lambda$ , where  $\ell$  is the optical thickness. Values of  $R$  around  $10^6$  to  $10^7$  can be achieved. It is impractical to increase  $\ell$  above  $\sim 5$  cm because the luminosity of the instrument is proportional to  $1/\ell$ . If higher

Table 2.4.5.1. Definition of Laue classes

Crystal system	Laue class	Point groups
Cubic	$C_1$ $C_2$	432, $\bar{4}3m$ , $m\bar{3}m$ 23, $\bar{3}m$
Hexagonal	$H_1$ $H_2$	622, $6mm$ , $\bar{6}2m$ , $6/mmm$ 6, 6, $6/m$
Tetragonal	$T_1$ $T_2$	422, $4mm$ , $\bar{4}2m$ , $4/mmm$ 4, 4, $4/m$
Trigonal	$R_1$ $R_2$	32, $3m$ , $\bar{3}m$ 3, $\bar{3}$
Orthorhombic	$O$	$mmm$ , $2mm$ , 222

### 3. SYMMETRY ASPECTS OF PHASE TRANSITIONS, TWINNING AND DOMAIN STRUCTURES

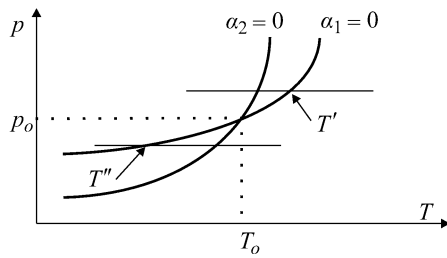


Fig. 3.1.2.3. Plots representative of the equations  $\alpha_1(p, T) = 0$  and  $\alpha_2(p, T) = 0$ . The simultaneous vanishing of these coefficients occurs for a single couple of temperature and pressure  $(p_0, T_0)$ .

$(T_0, p_0)$ . Let us consider, for instance, the situation depicted in Fig. 3.1.2.3. For  $p > p_0$ , on lowering the temperature,  $\alpha_1$  vanishes at  $T'$  and  $\alpha_2$  remains positive in the neighbourhood of  $T'$ . Hence, the equilibrium value of the set  $(d_x, d_y)$  remains equal to zero on either side of  $T'$ . A transition at this temperature will only concern a possible change in  $d_z^0$ .

Likewise for  $p$  below  $p_0$ , a transition at  $T''$  will only concern a possible change of the set of components  $(d_x^0, d_y^0)$ , the third component  $d_z$  remaining equal to zero on either sides of  $T''$ . Hence an infinitesimal change of the pressure (for instance a small fluctuation of the atmospheric pressure) from above  $p_0$  to below  $p_0$  will *modify qualitatively the nature of the phase transformation* with the direction of the displacement changing abruptly from  $z$  to the  $(x, y)$  plane. As will be seen below, the crystalline symmetries of the phases stable below  $T'$  and  $T''$  are different. This is a singular situation, of *instability*, of the type of phase transition, not encountered in real systems. Rather, the standard situation corresponds to pressures away from  $p_0$ , for which a slight change of the pressure does not modify significantly the direction of the displacement. In this case, one coefficient  $\alpha_i$  only vanishes and changes sign at the transition temperature, as stated above.

#### 3.1.2.2.5. Stable state below $T_c$ and physical anomalies induced by the transition

We have seen that either  $d_z$  or the couple  $(d_x, d_y)$  of components of the displacement constitute the order parameter of the transition and that the free energy needs only to be expanded as a function of the components of the order parameter. Below the transition, the corresponding coefficient  $\alpha_i$  is negative and, accordingly, the free energy, limited to its second-degree terms, has a maximum for  $\mathbf{d} = 0$  and no minimum. Such a truncated expansion is not sufficient to determine the equilibrium state of the system. The stable state of the system must be determined by positive terms of higher degrees. Let us examine first the simplest case, for which the order parameter coincides with the  $d_z$  component.

The same symmetry argument used to establish the form (3.1.2.1) of the Landau free energy allows one straightforwardly to assert the absence of a third-degree term in the expansion of  $F$  as a function of the order parameter  $d_z$ , and to check the effective occurrence of a fourth-degree term. If we assume that this simplest form of expansion is sufficient to determine the equilibrium state of the system, the coefficient of the fourth-degree term must be positive in the neighbourhood of  $T_c$ . Up to the latter degree, the form of the relevant contributions to the free energy is therefore

$$F = F_0(T, p) + \frac{\alpha(T - T_c)}{2} d_z^2 + \frac{\beta}{4} d_z^4. \quad (3.1.2.2)$$

In this expression,  $\alpha_1$ , which is an odd function of  $(T - T_c)$  since it vanishes and changes sign at  $T_c$ , has been expanded linearly. Likewise, the lowest-degree expansion of the function  $\beta(T - T_c)$  is a *positive constant* in the vicinity of  $T_c$ . The function  $F_0$ , which is the zeroth-degree term in the expansion, represents

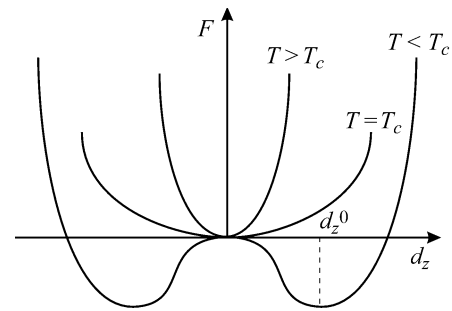


Fig. 3.1.2.4. Plots of the Landau free energy as a function of the order parameter, for values of the temperature above or below  $T_c$  or coincident with  $T_c$ . The shape of the plot changes qualitatively from a one-minimum plot to a two-minimum plot.

the normal 'background' part of the free energy. It behaves smoothly since it does not depend on the order parameter. A plot of  $[F(d_z) - F_0]$  for three characteristic temperatures is shown in Fig. 3.1.2.4.

The minima of  $F$ , determined by the set of conditions

$$\frac{\partial F}{\partial d_z} = 0; \quad \frac{\partial^2 F}{\partial d_z^2} > 0, \quad (3.1.2.3)$$

occur above  $T_c$  for  $d_z = 0$ , as expected. For  $T < T_c$  they occur for

$$d_z^0 = \pm \sqrt{\alpha \frac{(T_c - T)}{\beta}}. \quad (3.1.2.4)$$

This behaviour has a general validity: the order parameter of a transition is expected, in the framework of Landau's theory, to possess a square-root dependence as a function of the deviation of the temperature from  $T_c$ .

Note that one finds two minima corresponding to the same value of the free energy and opposite values of  $d_z^0$ . The corresponding upward and downward displacements of the  $M^+$  ion (Fig. 3.1.2.1) are distinct states of the system possessing the same stability.

Other physical consequences of the form (3.1.2.2) of the free energy can be drawn: absence of latent heat associated with the crossing of the transition, anomalous behaviour of the specific heat, anomalous behaviour of the *dielectric susceptibility* related to the order parameter.

The *latent heat* is  $L = T\Delta S$ , where  $\Delta S$  is the difference in entropy between the two phases at  $T_c$ . We can derive  $S$  in each phase from the equilibrium free energy  $F(T, p, d_z^0(T, p))$  using the expression

$$S = -\frac{dF}{dT} \Big|_{d_z^0} = -\left[ \frac{\partial F}{\partial T} \Big|_{d_z^0} + \frac{\partial F}{\partial d_z} \frac{d(d_z^0)}{dT} \Big|_{d_z^0} \right]. \quad (3.1.2.5)$$

However, since  $F$  is a minimum for  $d_z = d_z^0$ , the second contribution vanishes. Hence

$$S = -\frac{\alpha}{2} (d_z^0)^2 - \frac{\partial F_0}{\partial T}. \quad (3.1.2.6)$$

Since both  $d_z^0$  and  $(\partial F_0/\partial T)$  are continuous at  $T_c$ , there is no entropy jump  $\Delta S = 0$ , and *no latent heat at the transition*.

Several values of the specific heat can be considered for a system, depending on the quantity that is maintained constant. In the above example, the displacement  $\mathbf{d}$  of a positive ion determines the occurrence of an electric dipole (or of a macroscopic polarization  $\mathbf{P}$ ). The quantity  $\epsilon$ , which is thermodynamically conjugated to  $d_z$ , is therefore proportional to an electric field (the conjugation between quantities  $\eta$  and  $\zeta$  is expressed by the fact that infinitesimal work on the system has the form  $\zeta d\eta - cf$ .



### 3.1. STRUCTURAL PHASE TRANSITIONS

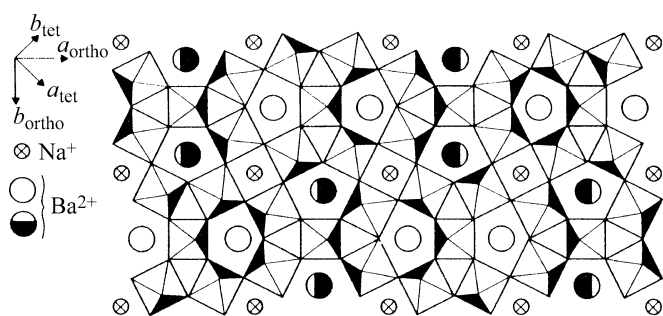


Fig. 3.1.5.12. Structure of the tungsten bronze barium sodium niobate  $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$  in its highest-temperature  $P4/mbm$  phase above 853 K.

with ribbons of such octahedra rather widely separated by the large ionic radius barium ions in the  $b$  direction. The resulting structure is, both magnetically and mechanically, rather two-dimensional, with easy cleavage perpendicular to the  $b$  axis and highly anisotropic electrical (ionic) conduction.

Most members of the  $\text{BaMF}_4$  family ( $M = \text{Mg, Zn, Mn, Co, Ni, Fe}$ ) have the same structure, which is that of orthorhombic  $C_{2v}$  ( $2mm$ ) point-group symmetry. These materials are all ferroelectric (or at least pyroelectric; high conductivity of some makes switching difficult to demonstrate) at all temperatures, with an ‘incipient’ ferroelectric Curie temperature extrapolated from various physical parameters (dielectric constant, spontaneous polarization *etc.*) to lie 100 K or more above the melting point (*ca.* 1050 K). The Mn compound is unique in having a low-temperature phase transition. The reason is that  $\text{Mn}^{+2}$  represents (Shannon & Prewitt, 1969) an end point in ionic size (largest) for the divalent transition metal ions Mn, Zn, Mg, Fe, Ni, Co; hence, the Mn ion and the space for it in the lattice are not a good match. This size mismatch can be accommodated by the r.m.s. thermal motion above room temperature, but at lower temperatures a structural distortion must occur.

This phase transition was first detected (Spencer *et al.*, 1970) *via* ultrasonic attenuation as an anomaly near 255 K. This experimental technique is without question one of the most sensitive in discovering phase transitions, but unfortunately it gives no direct information about structure and often it signals something that is not in fact a true phase transition (in  $\text{BaMnF}_4$  Spencer *et al.* emphasized that they could find no other evidence that a phase transition occurred).

Raman spectroscopy was clearer (Fig. 3.1.5.11*b*), showing unambiguously additional vibrational spectra that arise from a doubling of the primitive unit cell. This was afterwards confirmed directly by X-ray crystallography at the Clarendon Laboratory, Oxford, by Wondre (1977), who observed superlattice lines indicative of cell doubling in the  $bc$  plane.

The real structural distortion near 250 K in this material is even more complicated, however. Inelastic neutron scattering at Brookhaven by Shapiro *et al.* (1976) demonstrated convincingly that the ‘soft’ optical phonon lies not at  $(0, 1/2, 1/2)$  in the Brillouin zone, as would have been expected for the  $bc$ -plane cell doubling suggested on the basis of Raman studies, but at  $(0.39, 1/2, 1/2)$ . This implies that the actual structural distortion from the high-temperature  $C_{2v}^{12}$  ( $Cmc2_1$ ) symmetry does indeed double the primitive cell along the  $bc$  diagonal but in addition modulates the lattice along the  $a$  axis with a resulting repeat length that is incommensurate with the original (high-temperature) lattice constant  $a$ . The structural distortion microscopically approximates a rigid fluorine octahedra rotation, as might be expected. Hence, the chronological history of developments for this material is that X-ray crystallography gave the correct lattice structure at room temperature; ultrasonic attenuation revealed a possible phase transition near 250 K; Raman spectroscopy confirmed the transition and implied that it involved primitive

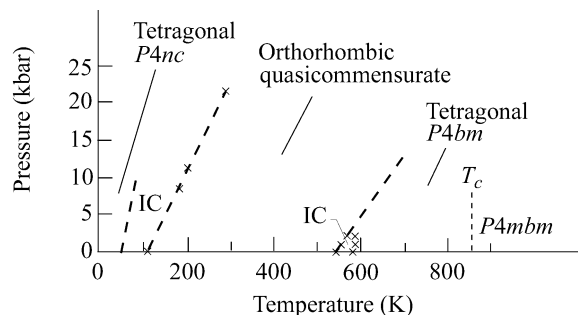


Fig. 3.1.5.13. Sequence of phases encountered with raising or lowering the temperature in barium sodium niobate.

cell doubling; X-ray crystallography confirmed directly the cell doubling; and finally neutron scattering revealed an unexpected incommensurate modulation as well. This interplay of experimental techniques provides a rather good model as exemplary for the field. For most materials, EPR would also play an important role in the likely scenarios; however, the short relaxation times for Mn ions made magnetic resonance of relatively little utility in this example.

#### 3.1.5.2.8. Barium sodium niobate

The tungsten bronzes represented by  $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$  have complicated sequences of structural phase transitions. The structure is shown in Fig. 3.1.5.12 and, viewed along the polar axis, consists of triangular, square and pentagonal spaces that may or may not be filled with ions. In barium sodium niobate, the pentagonal channels are filled with Ba ions, the square channels are filled with sodium ions, and the triangular areas are empty.

The sequence of phases is shown in Fig. 3.1.5.13. At high temperatures (above  $T_c = 853$  K) the crystal is tetragonal and paraelectric ( $P4/mbm = D_{4h}^2$ ). When cooled below 853 K it becomes ferroelectric and of space group  $P4bm = C_{4v}^2$  (still tetragonal). Between *ca.* 543 and 582 K it undergoes an incommensurate distortion. From 543 to *ca.* 560 K it is orthorhombic and has a ‘ $1q$ ’ modulation along a single orthorhombic axis. From 560 to 582 K it has a ‘tweed’ structure reminiscent of metallic lattices; it is still microscopically orthorhombic but has a short-range modulated order along a second orthorhombic direction and simultaneous short-range modulated order along an orthogonal axis, giving it an incompletely developed ‘ $2q$ ’ structure.

As the temperature is lowered still further, the lattice becomes orthorhombic but not incommensurate from 105–546 K; below 105 K it is incommensurate again, but with a microstructure quite different from that at 543–582 K. Finally, below *ca.* 40 K it becomes macroscopically tetragonal again, with probable space-group symmetry  $P4nc$  ( $C_{4v}^6$ ) and a primitive unit cell that is four times that of the high-temperature tetragonal phases above 582 K.

This sequence of phase transitions involves rather subtle distortions that are in most cases continuous or nearly continuous. Their elucidation has required a combination of experimental techniques, emphasizing optical birefringence (Schneck, 1982), Brillouin spectroscopy (Oliver, 1990; Schneck *et al.*, 1977; Tolédano *et al.*, 1986; Errandonea *et al.*, 1984), X-ray scattering, electron microscopy and Raman spectroscopy (Shawabkeh & Scott, 1991), among others. As with the other examples described in this chapter, it would have been difficult and perhaps impossible to establish the sequence of structures *via* X-ray techniques alone. In most cases, the distortions are very small and involve essentially only the oxygen ions.

#### 3.1.5.2.9. Tris-sarcosine calcium chloride (TSCC)

Tris-sarcosine calcium chloride has the structure shown in Fig. 3.1.5.14. It consists of sarcosine molecules of formula

## 3.2. Twinning and domain structures

BY V. JANOVEC, TH. HAHN AND H. KLAPPER

### 3.2.1. Introduction and history

*Twins* have been known for as long as mankind has collected minerals, admired their beauty and displayed them in museums and mineral collections. In particular, large specimens of contact and penetration twins with their characteristic re-entrant angles and simulated higher symmetries have caught the attention of mineral collectors, miners and scientists. *Twinning* as a special feature of crystal morphology, therefore, is a 'child' of mineralogy, and the terms and symbols in use for twinned crystals have developed during several centuries together with the development of mineralogy.

The first scientific description of *twinning*, based on the observation of re-entrant angles, goes back to Romé de l'Isle (1783). Haüy (1801) introduced symmetry considerations into twinning. He described *hemitropes* (twofold rotation twins) and *penetration twins*, and stated that the *twin face* is parallel to a possible crystal face. Much pioneering work was done by Weiss (1809, 1814, 1817/1818) and Mohs (1822/1824, 1823), who extended the symmetry laws of twinning and analysed the symmetry relations of many twins occurring in minerals. Naumann (1830) was the first to distinguish between twins with parallel axes (*Zwillinge mit parallelen Achsensystemen*) and twins with inclined (*crossed*) axes (*Zwillinge mit gekreuzten Achsensystemen*), and developed the mathematical theory of twins (Naumann, 1856). A comprehensive survey of the development of the concept and understanding of twinning up to 1869 is presented by Klein (1869).

At the beginning of the 20th century, several important mineralogical schools developed new and far-reaching ideas on twinning. The French school of Mallard (1879) and Friedel (1904) applied the lattice concept of Bravais to twinning. This culminated in the lattice classification of twins by Friedel (1904, 1926) and his introduction of the terms *macles par méridrie* (twinning by merohedry), *macles par pseudo-méridrie* (twinning by pseudo-merohedry), *macles par méridrie réticulaire* [twinning by reticular (lattice) merohedry] and *macles par pseudo-méridrie réticulaire* (twinning by reticular pseudo-merohedry). This concept of twinning was very soon taken up and further developed by Niggli in Zürich, especially in his textbooks (1919, 1920, 1924, 1941). The lattice theory of Mallard and Friedel was subsequently extensively applied and further extended by J. D. H. Donnay (1940), and in many later papers by Donnay & Donnay, especially Donnay & Donnay (1974). The Viennese school of Tschermak (1904, 1906), Tschermak & Becke (1915), and Tertsch (1936) thoroughly analysed the morphology of twins, introduced the *Kantennormalengesetz* and established the minimal conditions for twinning. The structural and energy aspects of twins and their boundaries were first accentuated and developed by Buerger (1945). Presently, twinning plays an important (but negative) role in crystal structure determination. Several sophisticated computer programs have been developed that correct for the presence of twinning in a small single crystal.

A comprehensive review of twinning is given by Cahn (1954); an extensive treatment of mechanical twinning is presented in the monograph by Klassen-Neklyudova (1964). A tensor classification of twinning was recently presented by Wadhawan (1997, 2000). Brief modern surveys are contained in the textbooks by Bloss (1971), Giacobozzo (1992) and Indenbom (see Vainshtein *et al.*, 1995), the latter mainly devoted to theoretical aspects. In previous volumes of *International Tables*, two articles on twin-

ning have appeared: formulae for the calculation of characteristic twin data, based on the work by Friedel (1926, pp. 245–252), are collected by Donnay & Donnay in Section 3 of Volume II of the previous series (Donnay & Donnay, 1972), and a more mathematical survey is presented by Koch in Chapter 1.3 of Volume C of the present series (Koch, 2004).

Independently from the development of the concept of twinning in mineralogy and crystallography, summarized above, the concept of *domain structures* was developed in physics at the beginning of the 20th century. This started with the study of *ferromagnetism* by Weiss (1907), who put forward the idea of a molecular field and formulated the hypothesis of differently magnetized regions, called *ferromagnetic domains*, that can be switched by an external magnetic field. Much later, von Hámos & Thiessen (1931) succeeded in visualizing magnetic domains by means of colloidal magnetic powder. For more details about magnetic domains see Section 1.6.4 of the present volume.

In 1921, Valasek (1921) observed unusual dielectric behaviour in Rochelle salt and pointed out its similarity with anomalous properties of ferromagnetic materials. This analogy led to a prediction of 'electric' domains, *i.e.* regions with different directions of spontaneous polarization that can be switched by an electric field. Materials with this property were called *Seignette electrics* (derived from the French, '*sel de Seignette*', denoting Rochelle salt). The term *seignettelectrics* is still used in Russian, but in English has been replaced by the term *ferroelectrics* (Mueller, 1935). Although many experimental and theoretical results gave indirect evidence for *ferroelectric domain structure* [for an early history see Cady (1946)], it was not until 1944 that Zwicker & Scherrer (1944) reported the first direct optical observation of the domain structure in ferroelectric potassium dihydrogen phosphate (KDP). Four years later, Klassen-Neklyudova *et al.* (1948) observed the domain structure of Rochelle salt in a polarizing microscope (see Klassen-Neklyudova, 1964, p. 27). In the same year, Blattner *et al.* (1948), Kay (1948) and Matthias & von Hippel (1948) visualized domains and domain walls in barium titanate crystals using the same technique.

These early studies also gave direct evidence of the influence of mechanical stress and electric field on domain structure. Further, it was disclosed that a domain structure exists only below a certain temperature, called the *Curie point*, and that the crystal structures below and above the Curie point have different point-group symmetries. The Curie point thus marks a structural phase transition between a *paraelectric phase* without a domain structure and a *ferroelectric phase* with a ferroelectric domain structure. Later, the term 'Curie point' was replaced by the more suitable expression *Curie temperature* or *transition temperature*.

The fundamental achievement in understanding phase transitions in crystals is the *Landau theory* of continuous phase transitions (Landau, 1937). Besides a thermodynamic explanation of anomalies near phase transitions, it discloses that any continuous phase transition is accompanied by a discontinuous decrease of crystal symmetry. In consequence, a phase with lower symmetry can always form a domain structure.

The basic role of symmetry was demonstrated in the pioneering work of Zheludev & Shuvalov (1956), who derived by simple crystallographic considerations the point groups of paraelectric and ferroelectric phases of all possible ferroelectric phase transitions and gave a formula for the number of ferroelectric domain states.

### 3.3. Twinning of crystals

BY TH. HAHN AND H. KLAPPER

In this chapter, the basic concepts and definitions of twinning, as well as the morphological, genetic and lattice classifications of twins, are presented. Furthermore, twin boundaries are discussed extensively. The effect of twinning in reciprocal space, *i.e.* on diffraction and crystal-structure determinations, is treated in Section 3.3.11. In the literature, the concept of twinning is very often used in a non-precise or ambiguous way. In order to clarify the terminology, this chapter begins with a section on the various kinds of crystal aggregates and intergrowths; in this context twinning appears as a special intergrowth of two or more crystals with well defined crystallographic orientation relations.

#### 3.3.1. Crystal aggregates and intergrowths

Minerals in nature and synthetic solid materials display different kinds of *aggregations*, in mineralogy often called *intergrowths*. In this chapter, we consider only aggregates of crystal grains of the same species, *i.e.* of the same (or nearly the same) chemical composition and crystal structure (*homophase* aggregates). Intergrowths of grains of different species (*heterophase* aggregates), *e.g.* heterophase bicrystals, epitaxy (two-dimensional oriented intergrowth on a surface), topotaxy (three-dimensional oriented precipitation or exsolution) or the paragenesis of different minerals in a rock or in a technical product are not treated in this chapter.

(i) *Arbitrary intergrowth*: Aggregation of two or more crystal grains with arbitrary orientation, *i.e.* without any systematic regularity. Examples are irregular aggregates of quartz crystals (*Bergkristall*) in a geode and intergrown single crystals precipitated from a solution. To this category also belong untextured polycrystalline materials and ceramics, as well as sandstone and quartzite.

(ii) *Parallel intergrowth*: Combination of two or more crystals with parallel (or nearly parallel) orientation of all edges and faces. Examples are dendritic intergrowths as well as parallel intergrowths of spinel octahedra (Fig. 3.3.1.1*a*) and of quartz prisms (Fig. 3.3.1.1*b*). Parallel intergrowths frequently exhibit re-entrant angles and are, therefore, easily misinterpreted as twins.

Two possible reasons for the formation of parallel intergrowths are mentioned:

(a) A smaller crystal has set down in parallel orientation on a growth face of an already existing crystal of the same species and has further grown together with its host. Fig. 3.3.1.1*a* suggests such a mechanism.

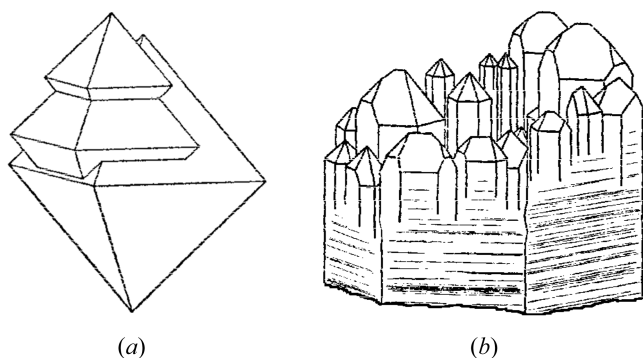


Fig. 3.3.1.1. Parallel intergrowth (a) of spinel octahedra and (b) of hexagonal quartz prisms. Part (a) after Phillips (1971, p. 172), part (b) after Tschermak & Becke (1915, p. 94).

(b) The growth of one or several faces of a crystal is inhibited by a layer of impurities or by foreign particles. By a local 'breaking down' of these obstacles, several parallel individual crystals may appear and grow together during further growth. This mechanism is suggested for Fig. 3.3.1.1*b*).

In this context the term *mosaic crystal* must be mentioned. It was introduced in the early years of X-ray diffraction in order to characterize the perfection of a crystal. A mosaic crystal consists of small blocks (size typically in the micron range) with orientations deviating only slightly from the average orientation of the crystal; the term 'lineage structure' is also used for very small scale parallel intergrowths (Buerger, 1934, 1960*a*, pp. 69–73).

(iii) *Bicrystals*: This term is mainly used in metallurgy. It refers to the (usually synthetic) intergrowth of two single crystals with a well defined orientation relation. A bicrystal contains a *grain boundary*, which in general is also well defined. Usually, homophase bicrystals are synthesized in order to study the structure and properties of grain boundaries. An important tool for the theoretical treatment of bicrystals and their interfaces is the *coincidence-site lattice* (CSL). A brief survey of bicrystals is given in Section 3.2.2; a comparison with twins and domain structures is provided by Hahn *et al.* (1999).

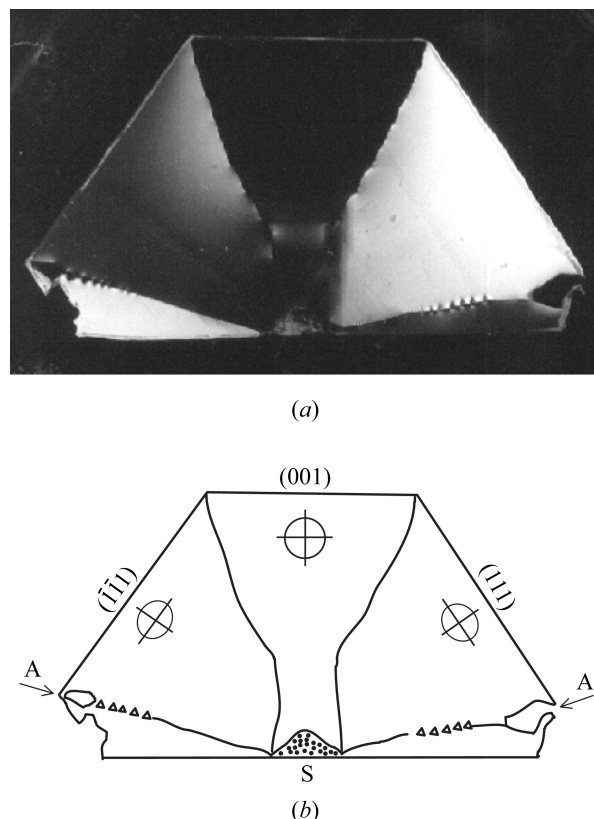


Fig. 3.3.1.2. (a) Optical anomaly of a cubic mixed (K,NH<sub>4</sub>)-alum crystal grown from aqueous solution, as revealed by polarized light between crossed polarizers: (110) plate, 1 mm thick, horizontal dimension about 4 cm. (b) Sketch of growth sectors and their boundaries of the crystal plate shown in (a). The {111} growth sectors are optically negative and approximately uniaxial with their optical axes parallel to their growth directions {111} [birefringence  $\Delta n$  up to  $5 \times 10^{-5}$ ; Shtukenberg *et al.* (2001)]. The (001) growth sector is nearly isotropic ( $\Delta n < 10^{-6}$ ). Along the boundaries A between {111} sectors a few small {110} growth sectors (resulting from small {110} facets) have formed during growth. S: seed crystal.

### 3. SYMMETRY ASPECTS OF PHASE TRANSITIONS, TWINNING AND DOMAIN STRUCTURES

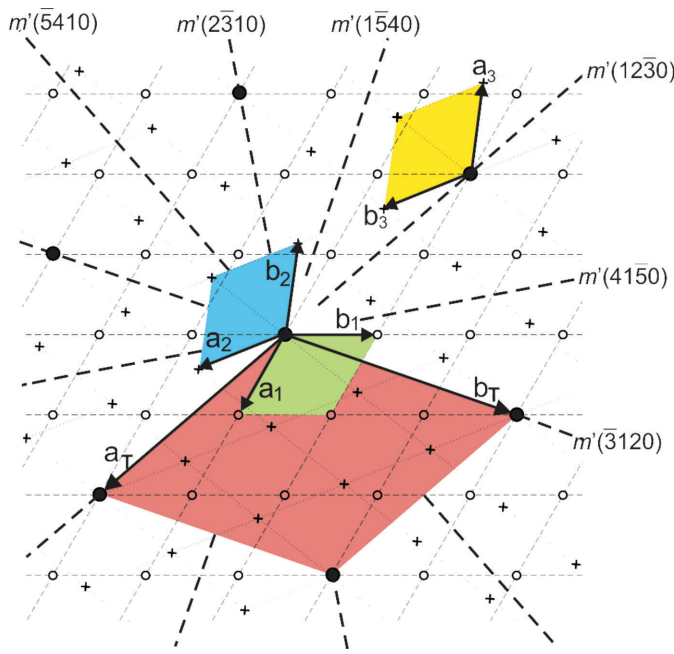


Fig. 3.3.11.5. Hexagonal lattices ( $a$ - $b$  planes, common  $c$  axis pointing upwards) of twin domain I (start domain, lattice points small circles, right-handed green unit cell  $\mathbf{a}_1, \mathbf{b}_1, \mathbf{c}_1$ ), of the  $\Sigma 7$  twin-related domain II (small crosses, left-handed blue unit cell  $\mathbf{a}_2, \mathbf{b}_2, \mathbf{c}_2$ ) and of the  $\Sigma 7$  coincidence lattice (large black points, right-handed red unit cell  $\mathbf{a}_T, \mathbf{b}_T, \mathbf{c}_T$ ). The six alternative twin reflection planes  $m'(12\bar{3}0)$ ,  $m'(\bar{3}120)$ ,  $m'(2\bar{3}10)$ ,  $m'(\bar{5}410)$ ,  $m'(\bar{1}540)$  and  $m'(41\bar{5}0)$  are indicated by dashed lines. The coordinate axes  $\mathbf{a}_2, \mathbf{b}_2, \mathbf{c}_2$  of domain II (blue) are defined by the reflection plane  $m'(12\bar{3}0)$ . The right-handed yellow unit cell  $\mathbf{a}_3, \mathbf{b}_3, \mathbf{c}_3$  of domain II is obtained from  $\mathbf{a}_1, \mathbf{b}_1, \mathbf{c}_1$  by a clockwise rotation of  $\varphi = 120^\circ + 2 \arcsin [(1/2)(3/7)^{1/2}] = 120^\circ + 38.2^\circ = 158.2^\circ$  around the hexagonal  $c$  axis. This cell is commonly used in structure determinations. (From Hahn & Klapper, 2012.)

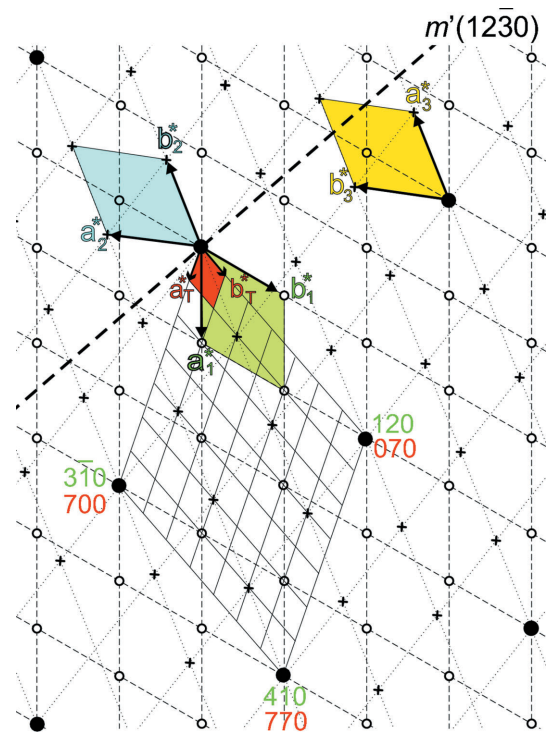


Fig. 3.3.11.6. Reciprocal hexagonal lattices ( $hk0$  lattice planes) of twin domain I (start domain, lattice points small circles) and of the  $\Sigma 7$  twin-related domain II (small crosses). The reciprocal lattice of the (direct-space)  $\Sigma 7$  coincidence lattice is represented by the grid of small rhombuses. The unit cells, their handedness and their colours correspond to those of the direct lattices in Fig. 3.3.11.5. In the large cell formed by the four reciprocal coincidence points 000,  $3\bar{1}0$ , 410, 120 (in terms of  $\mathbf{a}_1^*, \mathbf{b}_1^*$ ) or 000, 700, 770, 070 (in terms of  $\mathbf{a}_T^*, \mathbf{b}_T^*$ ) there are six 'single' points of twin domains I and II each, one 'coincident' point 000 and, with reference to  $\mathbf{a}_T^*, \mathbf{b}_T^*$ , 36 'extinct' reciprocal points (cf. Table 3.3.11.1). These strange 'non-space-group extinctions' are characteristic of the  $\Sigma 7$  twin law. (From Hahn & Klapper, 2012.)

systems, hexagonal  $P$  and rhombohedral  $R$  lattices) are the hexagonal equivalents of the tetragonal  $\Sigma 5$  twins treated above. Hence, many features agree: the  $\Sigma 7$  twins are also parallel  $c$ -axes twins, *i.e.* they preserve the hexagonal or trigonal axis and, thus, the twinning is 'two-dimensional' (Fig. 3.3.11.5). Twins with inclined main axes have been derived by Grimmer (1989*a*), but real examples have not yet been observed.

The smallest possible lattice index is  $\Sigma = h^2 + hk + k^2 = 7$  or  $\Sigma = (h^2 + hk + k^2)/3 = 21/3 = 7$  (similarly for  $\Sigma = u^2 - uv + v^2$ ) for a twin with twin symmetry (reduced oriented composite symmetry)  $6/m\ 2/m\ 2/m'$  and the following four twin laws, represented by:

- $m'\{12\bar{3}0\}$ ,  $2'\langle 450 \rangle$  (second position of the twin point-group symbol),
- $m'\{5410\}$ ,  $2'\langle 2\bar{1}0 \rangle$  (third position of the twin point-group symbol).

In each of the two *hexagonal* centrosymmetric point groups  $6/m$  and  $6/m\ 2/m\ 2/m$  these four twin laws form *one* twin law, whereas in the six noncentrosymmetric point groups (structural settings) they combine in different ways into *two* twin laws.

In the three *trigonal* centrosymmetric point groups (structural settings)  $\bar{3}$ ,  $\bar{3}2/m1$  and  $\bar{3}12/m$ , they combine into two twin laws each, whereas in the remaining five trigonal structural settings all four twin laws are different, leading to 14 hexagonal and 26 trigonal possible  $\Sigma 7$  twins. Details of these twin cases are presented in Table 10 of Klapper & Hahn (2012).

The reciprocal lattice of the hexagonal  $\Sigma 7$  twins is shown in Fig. 3.3.11.6. As for the  $\Sigma 5$  twins, it confirms the data in Table 3.3.11.1: the  $7 \times 7$  cell formed by the coincident lattice points 000, 700, 770, 070 contains one 'doubly coincident' point 000, six 'single' points of twin domains D(I) and D(II) each and, if referred to  $\mathbf{a}_T^*$  and  $\mathbf{b}_T^*$ , 36 'doubly extinct' points.

Section 6 and Appendix C2 of the paper by Klapper & Hahn (2012) contains full details of the hexagonal  $\Sigma 7$  twins and their

treatment in diffraction and structure work. Twins of this kind have not been found so far. This also applies to the  $\Sigma 7$  twins of crystals with a rhombohedral  $R$  lattice [the frequent rhombohedral  $\Sigma 3$  twins are treated above under (ii)]. Their (somewhat complicated) twin phenomena are also described in the above-mentioned paper.

Beyond the 'starting type'  $\Sigma 7$ , the following twins also belong to this family:

- $\Sigma 13$  with  $m'\{31\bar{4}0\}$  or  $2'\langle 140 \rangle$  (second position of the point-group symbol),
- $\Sigma 19$  with  $m'\{32\bar{5}0\}$  or  $2'\langle 250 \rangle$  (second position of the point-group symbol), similarly for higher  $\Sigma$  values.

Twins of this hexagonal/trigonal  $\Sigma m$  'family' are not known.

#### 3.3.11.5. Pseudo-merohedral twins

##### 3.3.11.5.1. General remarks

This type of twins includes both pseudo-merohedral  $\Sigma 1$  and  $\Sigma m > 1$  twins. It refers to small deviations from strict full or partial lattice coincidence of the twin partners. Pseudo-merohedral twins occur if metrical (but not necessary structural) pseudosymmetries occur in a crystal and, hence, the twin element belongs to the symmetry of a higher crystal system. Frequently occurring typical examples are monoclinic crystals with the angle  $\beta$  very close to  $90^\circ$  (simulating an orthorhombic crystal) or with approximately  $a = c$  (simulating a  $B$ -centred orthorhombic crystal), orthorhombic crystals with nearly  $bla \approx \sqrt{3}$  (simulating a hexagonal crystal, *cf.* examples below), or a tetragonal crystal with  $cla \approx 1$  (simulating a cubic crystal). In contrast to twins by strict  $\Sigma 1$  merohedry the twin operation is *not* a symmetry operation of the holohedry of the untwinned crystal. Thus the

## 3.4. Domain structures

BY V. JANOVEC AND J. PŘÍVRATSKÁ

### 3.4.1. Introduction

#### 3.4.1.1. Basic concepts

It was demonstrated in Section 3.1.2 that a characteristic feature of structural phase transitions connected with a lowering of crystal symmetry is an anomalous behaviour near the transition, namely unusually large values of certain physical properties that vary strongly with temperature. In this chapter, we shall deal with another fundamental feature of structural phase transitions associated with symmetry lowering: the formation of a non-homogeneous, textured low-symmetry phase called a *domain structure*.

When a crystal homogeneous in the *parent* (prototypic, high-symmetry) phase undergoes a phase transition into a *ferroic* low-symmetry phase with lower point-group symmetry, then this ferroic phase is almost always formed as a non-homogeneous structure consisting of homogeneous regions called *domains* and contact regions between domains called *domain walls*. All domains have the same or the enantiomorphous crystal structure of the ferroic phase, but this structure has in different domains a different orientation, and sometimes also a different position in space. When a domain structure is observed by a measuring instrument, different domains can exhibit different tensor properties, different diffraction patterns and can differ in other physical properties. The domain structure can be visualized optically (see Fig. 3.4.1.1) or by other experimental techniques. Powerful high-resolution electron microscopy (HREM) techniques have made it possible to visualize atomic arrangements in domain structures (see Fig. 3.4.1.2). The appearance of a domain structure, detected by any reliable technique, provides the simplest unambiguous experimental proof of a structural phase transition.

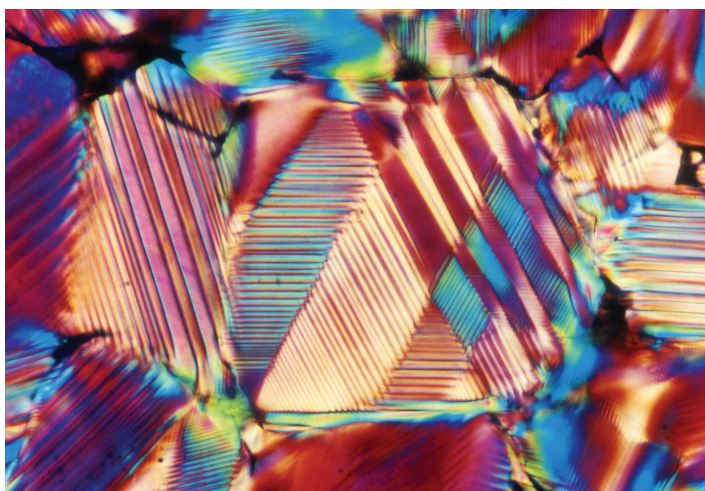


Fig. 3.4.1.1. Domain structure of tetragonal barium titanate ( $\text{BaTiO}_3$ ). A thin section of barium titanate ceramic observed at room temperature in a polarized-light microscope (transmitted light, crossed polarizers). Courtesy of U. Täffner, Max-Planck-Institut für Metallforschung, Stuttgart. Different colours correspond to different ferroelastic domain states, connected areas of the same colour are ferroelastic domains and sharp boundaries between these areas are domain walls. Areas of continuously changing colour correspond to gradually changing thickness of wedge-shaped domains. An average distance between parallel ferroelastic domain walls is of the order of 1–10  $\mu\text{m}$ .

Under the influence of external fields (mechanical stress, electric or magnetic fields, or combinations thereof), the domain structure can change; usually some domains grow while others decrease in size or eventually vanish. This process is called *domain switching*. After removing or decreasing the field a domain structure might not change considerably, *i.e.* the form of a domain pattern depends upon the field history: the domain structure exhibits *hysteresis* (see Fig. 3.4.1.3). In large enough fields, switching results in a reduction of the number of domains. Such a procedure is called *detwinning*. In rare cases, the crystal may consist of one domain only. Then we speak of a *single-domain crystal*.

There are two basic types of domain structures:

(i) Domain structures with one or several systems of parallel plane domain walls that can be observed in an optical or electron microscope. Two systems of perpendicular domain walls are often visible (see Fig. 3.4.1.4). In polarized light, domains exhibit different colours (see Fig. 3.4.1.1) and in diffraction experiments splitting of reflections can be observed (see Fig. 3.4.3.9). Domains can be switched by external mechanical stress. These features are typical for a *ferroelastic domain structure* in which neighbouring domains differ in mechanical strain (deformation). Ferroelastic domain structures can appear only in ferroelastic phases, *i.e.* as a result of a phase transition characterized by a decrease in the number of independent strain components (see Table 3.4.2.2).

(ii) Domain structures that are not visible using a polarized-light microscope and in whose diffraction patterns no splitting of reflections is observed. Special methods [*e.g.* etching, deposition of liquid crystals (see Fig. 3.4.1.5), electron or atomic force microscopy, or higher-rank optical effects (see Fig. 3.4.3.3)] are needed to visualize domains. Domains have the same strain and cannot usually be switched by an external mechanical stress. Such domain structures are called *non-ferroelastic domain structures*. They appear in all non-ferroelastic phases resulting from symmetry lowering that preserves the number of independent strain components (see Table 3.4.2.2).

Another important kind of domain structure is a *ferroelectric domain structure*, in which domains differ in the direction of the

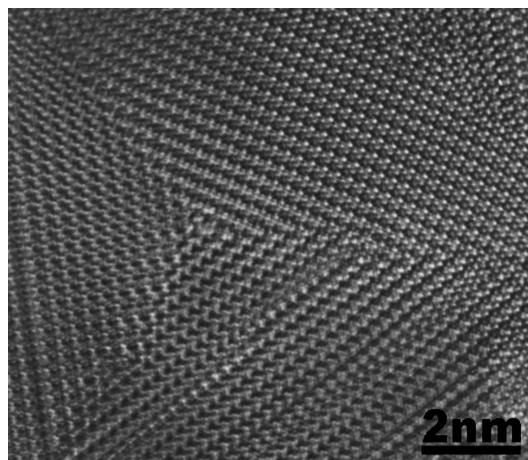


Fig. 3.4.1.2. Domain structure of a  $\text{BaGa}_2\text{O}_4$  crystal seen by high-resolution transmission electron microscopy. Parallel rows are atomic layers. Different directions correspond to different ferroelastic domain states of domains, connected areas with parallel layers are different ferroelastic domains and boundaries between these areas are ferroelastic domain walls. Courtesy of H. Lemmens, EMAT, University of Antwerp.

### 3.4. DOMAIN STRUCTURES

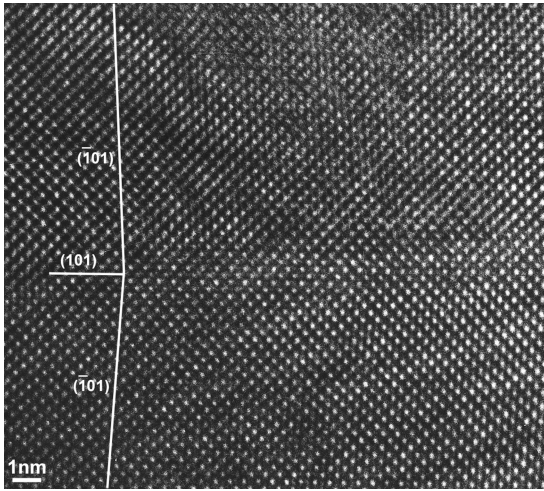


Fig. 3.4.3.6. High-resolution electron microscopy image of a ferroelastic twin in the orthorhombic phase of  $\text{WO}_3$ . Courtesy of H. Lemmens, EMAT, University of Antwerp.

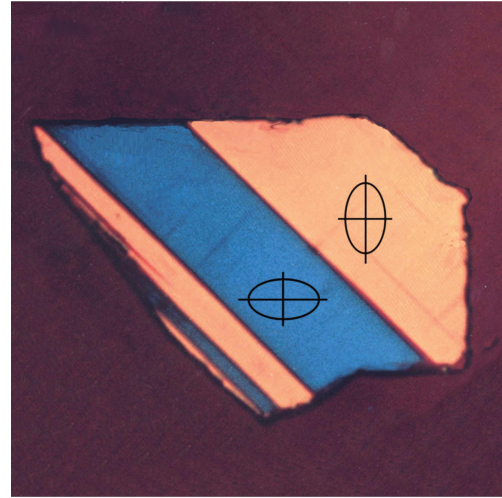
angle between these planes equals  $2\omega$ , where  $\omega$  is the shear angle (obliquity) of the ferroelastic twin.

Disorientations of domain states in a ferroelastic twin bring about a deviation of the optical indicatrix from a strictly perpendicular position. Owing to this effect, ferroelastic domains exhibit different colours in polarized light and can be easily visualized. This is illustrated for a domain structure of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  in Fig. 3.4.3.7. The symmetry descent  $G = 4_z/m_z m_x m_y \supset m_x m_y m_z = F_1 = F_2$  gives rise to two ferroelastic domain states  $\mathbf{R}_1$  and  $\mathbf{R}_2$ . The twinning group  $K_{12}$  of the non-trivial domain pair  $(\mathbf{R}_1, \mathbf{R}_2)$  is

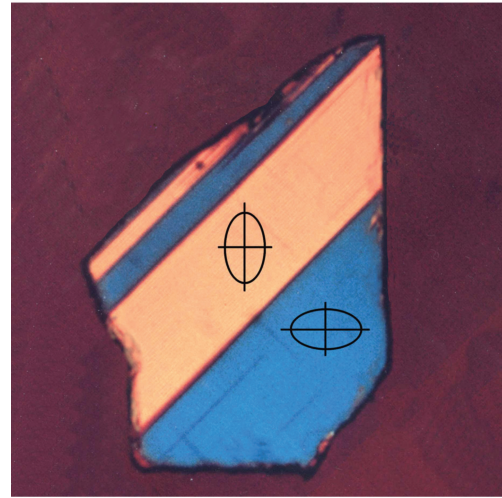
$$K_{12}[m_x m_y m_z] = J_{12}^* = m_x m_y m_z \cup 4_z^* \{2_x m_y m_z\} = 4_z^* / m_z m_x m_{xy}^*. \quad (3.4.3.61)$$

The colour of a domain state observed in a polarized-light microscope depends on the orientation of the index ellipsoid (indicatrix) with respect to a fixed polarizer and analyser. This index ellipsoid transforms in the same way as the tensor of spontaneous strain, *i.e.* it has different orientations in ferroelastic domain states. Therefore, different ferroelastic domain states exhibit different colours: in Fig. 3.4.3.7, the blue and pink areas (with different orientations of the ellipse representing the spontaneous strain in the plane of figure) correspond to two different ferroelastic domain states. A rotation of the crystal that does not change the orientation of ellipses (*e.g.* a  $180^\circ$  rotation about an axis parallel to the fourfold rotation axis) does not change the colours (ferroelastic domain states). If one neglects disorientations of ferroelastic domain states (see Section 3.4.3.6) – which are too small to be detected by polarized-light microscopy – then none of the operations of the group  $F_1 = F_2 = m_x m_y m_z$  change the single-domain ferroelastic domain states  $\mathbf{R}_1, \mathbf{R}_2$ , hence there is no change in the colours of domain regions of the crystal. On the other hand, all operations with a star symbol (operations lost at the transition) exchange domain states  $\mathbf{R}_1$  and  $\mathbf{R}_2$ , *i.e.* also exchange the two colours in the domain regions. The corresponding permutation is a transposition of two colours and this attribute is represented by a star attached to the symbol of the operation. This exchange of colours is nicely demonstrated in Fig. 3.4.3.7 where a  $-90^\circ$  rotation is accompanied by an exchange of the pink and blue colours in the domain regions (Schmid, 1991, 1993).

It can be shown (Shuvalov *et al.*, 1985; Dudnik & Shuvalov, 1989) that for small spontaneous strains the amount of shear  $s$  and the angle  $\omega$  can be calculated from the second invariant  $\Lambda_2$  of the differential tensor  $\Delta u_{ik}$ :



(a)



(b)

Fig. 3.4.3.7. Ferroelastic twins in a very thin  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  crystal observed in a polarized-light microscope. Courtesy of H. Schmid, Université de Geneve.

$$s = 2\sqrt{-\Lambda_2}, \quad (3.4.3.62)$$

$$\omega = \sqrt{-\Lambda_2}, \quad (3.4.3.63)$$

where

$$\Lambda_2 = \left| \begin{array}{cc} \Delta u_{11} & \Delta u_{12} \\ \Delta u_{21} & \Delta u_{22} \end{array} \right| + \left| \begin{array}{cc} \Delta u_{22} & \Delta u_{23} \\ \Delta u_{32} & \Delta u_{33} \end{array} \right| + \left| \begin{array}{cc} \Delta u_{11} & \Delta u_{13} \\ \Delta u_{31} & \Delta u_{33} \end{array} \right|. \quad (3.4.3.64)$$

In our example, where there are only two nonzero components of the differential spontaneous strain tensor [see equation (3.4.3.58)], the second invariant  $\Lambda_2 = -(\Delta u_{11} \Delta u_{22}) = -(u_{22} - u_{11})^2$  and the angle  $\omega$  is

$$\omega = \pm |u_{22} - u_{11}|. \quad (3.4.3.65)$$

In this case, the angle  $\omega$  can also be expressed as  $\omega = \pi/2 - 2 \arctan a/b$ , where  $a$  and  $b$  are lattice parameters of the orthorhombic phase (Schmid *et al.*, 1988).

The shear angle  $\omega$  ranges in ferroelastic crystals from minutes to degrees (see *e.g.* Schmid *et al.*, 1988; Dudnik & Shuvalov, 1989).

Each equally deformed plane gives rise to two compatible domain walls of the same orientation but with opposite sequence of domain states on each side of the plane. We shall use for a *simple domain twin* with a planar wall a symbol  $(\mathbf{R}_1^+ | \mathbf{n} | \mathbf{R}_2^-)$  in which  $\mathbf{n}$  denotes the normal to the wall. The bra-ket symbol  $( | )$  and  $( | )$  represents the half-space domain regions on the negative