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Orbital ordering and multiferroics

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Chapter 2

A double approach

2.1 Experimental approach

2.1.1 Powder Diffraction versus Single crystal diffraction

Introduction

Since the discovery of diffraction, single crystal data collection has been generally used to collect integrated intensity whereas powder diffraction has been regarded as a more applied technique for phase identification and quantitative phase analysis. The development of the Rietveld method has changed this statement. Powder diffraction is nowadays a powerful tool for structure determination. Moreover, often polycrystalline samples (powders) are easier to obtain than single crystals, especially in the case of incongruent melting compounds.

Comparison

The great advantage of powder diffraction is that it does not require the growing and mounting of a single crystal. For neutron diffraction, a technique that requires larger samples than X-Ray diffraction, this is a more important consideration than for its X-ray equivalent. Powders are very much the standard for neutron diffraction, and single crystal work the exception. While powder diffraction allows better statistics, single crystal work one strongly depends on the single tiny crystal that is selected, to do all analysis. The great disadvantage of powder diffraction is that the three dimensional information of the reciprocal space of a crystal is projected into a one dimensional diffractogram. Nevertheless, powder diffraction is a widely used technique. Powder diffraction allows various in situ experiments to be carried out, and also the characterization of mixed phase samples, which is clearly impossible with single crystals. We can summarize the advantages and inconveniences of powder and single crystal diffraction in table 2.1.

| Single crystal diffraction | Powder diffraction |
|---|---|
| Determination of the crystal structure with high precision and accuracy | Identification of compounds or mixtures of different compounds |
| Information on ordering in crystals | Investigations on homogeneity |
| Information on thermal motion and dynamics in crystals | Information on stress, strain and crystal size |
| Very precise bond lengths | Quantitative phase analysis |
| Imprecise for cell parameters Precise in fractional coordinates | Determination of the crystal structure (Usually not as precise as from single crystal structure analysis) |

Table 2.1: *Advantages and inconveniences of powder and single crystal diffraction*

2.1.2 Single crystal growth

Introduction

The fabrication of single crystals is very important for both fundamental research and industrial purposes [1]. Single crystals can be obtained via various methods. They can be classified in three main categories: crystal growth from the melt, crystal growth from solution and chemical vapor transport. Each of these methods covers several kinds of particular techniques. However there are four main techniques used for growing transition metal oxides: flux (high temperature solution), the Bridgman method, the Czochralski method or by the "floating zone technique" (growth from the melt). All the single crystals presented in this thesis were grown by the floating zone technique.

Growth using Floating Zone Furnace

The floating zone technique is based on the zone melting principle. It is the same principle which is used also for the Bridgman and Czochralski methods. Zone melting has been developed initially for purification. Thus the Floating Zone Furnace gives rise to very pure single crystals. Moreover, as an advantage to the other zone melting method, there is no use of crucibles reducing possible contamination. In addition, a flux can be used for incongruent melting materials. While most of the optimal growth rates for metals lie between 0.5 and 15 cm/h, this value is reduced to 5 mm/h for transition metal oxides.

The floating zone mirror furnace that we have used for the single crystal growth is presented in figure 2.1. It is a four mirror floating zone furnace from Crystal Systems Inc. with halogen lamps having a power of 1500W each.

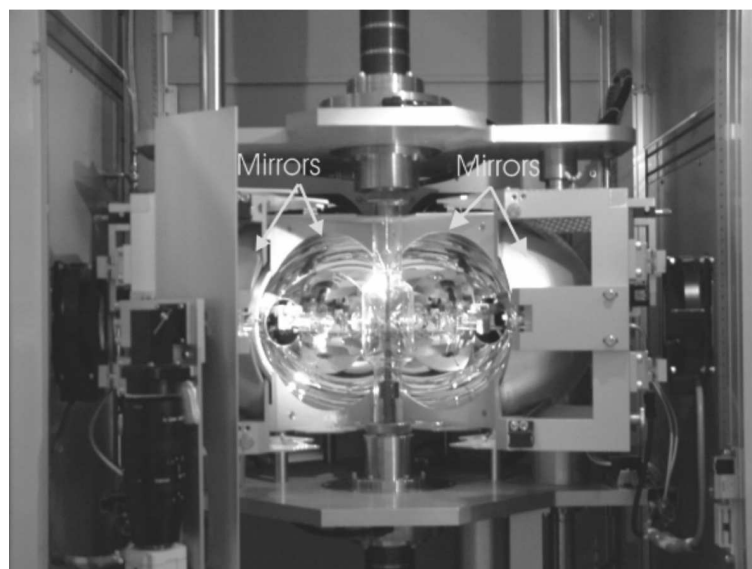


Figure 2.1: *The four mirror floating zone furnace that we used (Crystal Systems Inc., model n° FZ-T-1000-H-VI-VP).*

2.1.3 X-ray and neutron diffraction

Synchrotron versus laboratory sources for X-ray diffraction

All the standard laboratory sources used for X-ray diffraction experiments generate radiation using the same physical principles but can vary in their technical details. In our case, we have been using a Bragg-Brentano geometry using a sealed tube generator. The tube of X-rays is made from a source of electrons and a metallic cathode put in the chamber under high vacuum. The source of electrons is a filament of tungsten heated by an electric current, which expels electrons by the thermic effect. A high voltage from 40kV to 60kV is applied between the source of electrons (cathode) and the metallic anode and accelerates the electrons. Due to the way in which radiation is produced, only a discrete number of wavelengths and a broad background are available. For conventional X-ray diffraction, we have been using K_{α} of copper.

The generation of X-rays in a synchrotron radiation source involves a different technology. From mechanics and the Maxwell equations, it is well known that charged particles moving under the influence of an accelerating field emit electromagnetic radiation. This radiation can be used for diffraction purpose if the charged particles have a high acceleration corresponding to a speed close to the speed of light. This is realized in a synchrotron radiation facility where the charged particles (electrons or positrons) are kept circulating within an evacuated cavity on a closed path (the ring) by a num-

ber of curved magnets (the bending magnets). The different beamlines used for the different experiments are tangential to the particle trajectory. The advantage of such facility is the very bright source which is available and the possibility to tune the wavelength to the value required for a particular experiment.

Neutron diffraction

Neutron beams are produced by nuclear reactions, such as nuclear fission or fusion, or by spallation of nuclei by accelerated particles. Since for the moment nuclear fusion cannot be controlled sufficiently to produce stable neutron sources, all neutron centers use nuclear reactors (fission) and spallation sources. Spallation is the process in which a heavy nucleus emits a large number of nucleons as a result of being hit by a high-energy proton.

A number of properties of the neutron make it very useful for the study of solids. Since, neutrons are uncharged particles and of small dimensions (about 10^{-4} the size of an atom), they have a very penetrating power. The atomic scattering factors for X-rays increase throughout the periodic table (increase of the number of electrons) while it is not the case for neutrons. For neutrons, although there is a small increase of nuclear scattering factor with the mass number of the element, it is largely hidden by resonance effects which vary in a seemingly arbitrary fashion from atom to atom. As a result, the neutron scattering factors for different nuclei are in general all of the same order within a factor 4. The difference between the relative size of cross-sections (scattering factor) for X-ray and neutron is illustrated in figure 2.2.

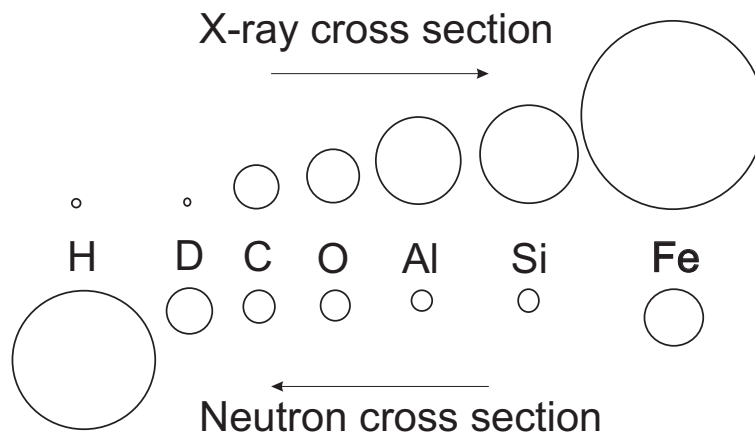


Figure 2.2: *Difference between the relative sizes of the cross-sections between X-ray and neutron for some elements.*

As a consequence, neutron diffraction is more sensitive to the light atoms like oxygen or hydrogen than X-ray diffraction. In this respect, these two

techniques are complementary. Another main difference between X-ray and neutron is related to the size of the electron cloud/nucleus. While the electron cloud has dimensions of about 1 Å, which is comparable with the X-ray wavelength, the radius of a nucleus is about 4 orders of magnitude smaller. It results that the nucleus may be considered as a point scatterer and there will be no decrease with θ of the neutron scattering factor. An additional property of the neutron is that it carries a spin and, consequently, once it interacts with the nuclei of the sample studied, it gives information about the magnetic properties.

2.1.4 Magnetometer SQUID

SQUIDs ("Superconducting Quantum Interferometer Device") enable to measure very small magnetic fields; SQUIDs are very sensitive sensors for magnetic fluxes. SQUIDs are used in the fields of electronics to biomagnetism; in addition to magnetic fluxes other physical values can be measured if they can be adapted to the magnetic flux. Attainable sensitivities of flux densities (10^{-14}T), of electrical current (10^{-12} A) and of electrical resistance ($10^{-12}\Omega$) reflect the high accuracy of a SQUID. The working principle of a SQUID is based on the quantum interference of wave functions that describe the state of the superconducting charge carriers, the so-called Cooper pairs. Each Cooper pair can be treated as a single particle with a mass and charge twice that of a single electron, whose velocity is that of the center of mass of the pair. A SQUID is based on an interferometer loop in which two weak links (Josephson contacts) are established. A weak link is realized by interrupting a superconductor by a very thin insulating barrier. The function of the SQUID is to link the quantum mechanical phase difference of the Cooper pairs wave functions over a weak link with the magnetic flux penetrating the interferometer loop.

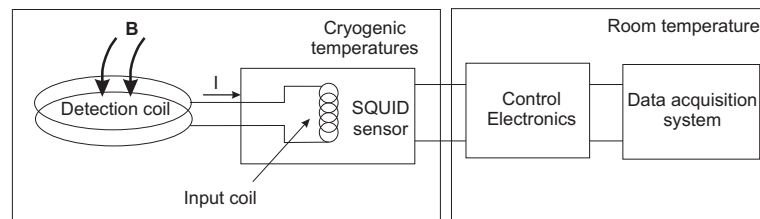


Figure 2.3: Scheme of a SQUID magnetometer.

The components of a SQUID magnetometer (Fig. 2.3) typically consist of the following: a detection coil, which senses changes in the external magnetic field and transforms them into an electrical current; an input coil which transforms the resulting current into a magnetic flux in the SQUID sensor; electronics which transform the applied flux into a room temperature

voltage output; and acquisition hardware and software for acquiring, storing and analyzing data. Both the SQUID amplifier and the detection coils are superconducting devices. Thus some type of refrigerant (liquid helium or liquid nitrogen) or refrigeration device (cryocooler) is needed to maintain the SQUID and detection coil in the superconducting state. Additional signal conditioning electronics may be needed to improve signal-to-noise. We use a MPMS (Magnetic Property Measurement System based on SQUID) from Quantum Design having the following characteristics: $H_{max}=7T$ and $\Delta T=1.8K-350K$.

2.1.5 Dielectric Properties

Capacitance measurement

The absolute complex permittivity of a material is represented by the symbol ε , where $\varepsilon = \varepsilon' - j\varepsilon''$ [2]. This is related to the dimensionless relative complex permittivity ε_r , where $\varepsilon_r = \varepsilon'_r - j\varepsilon''_r$, by the expression $\varepsilon = \varepsilon_0 \varepsilon_r$, ε_0 being the permittivity of free space, a fixed constant given approximately by $\varepsilon_0 = 8.85 \times 10^{-12} \text{F.m}^{-1}$. In general, ε depends on temperature and, to a lesser extent, pressure. It is also frequency dependent, although ε' and ε'' cannot vary independently with frequency, since their frequency variations are connected through the Kramers-Krönig relationship ($\varepsilon'(\omega) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\varepsilon''(x)}{x-\omega} dx$): a drop in ε' with increasing frequency is necessarily associated with a peak in ε'' . Except for exceedingly high applied fields, ε is independent of the magnitude of the applied electric field for all dielectric materials used in practice, excluding ferroelectrics.

A capacitor filled with a dielectric material has a real capacitance ε'_r times greater than would have a capacitor with the same electrodes in vacuum. The dielectric filled capacitor would also have a power dissipation W per unit volume at each point when, resulting from an applied voltage, a sinusoidal electric field of frequency f and root mean square value E exists at that point. This power dissipation is given by $W = 2\pi f E^2 \varepsilon''$. Thus ε'' is a measure of the energy dissipation per period, and for this reason it is known as the loss-factor.

The complex permittivity is often represented in the Argand plane with ε' as abscissa and ε'' as ordinate, giving a curve with frequency as parameter. This curve represents the complex conjugate ε^* of the complex permittivity where $\varepsilon^* = \varepsilon' + j\varepsilon''$. The segment to the origin makes an angle δ with the abscissa, such that $\tan(\delta) = \varepsilon''/\varepsilon'$. Thus W may be rewritten as $W = 2\pi f E^2 \varepsilon' \tan(\delta)$. Hence δ is known as the loss angle, and $\tan(\delta)$ is known as the loss tangent.

Capacitance is a measure of the amount of electric charge (Q) stored (or separated) for a given electric potential (V).

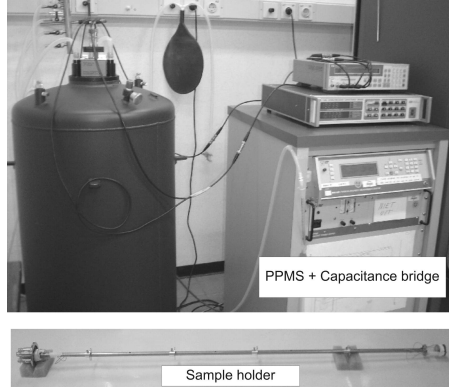


Figure 2.4: *Experimental set-up used to measure capacitance.*

$$C = \frac{Q}{V} \quad (2.1)$$

In a capacitor, there are two conducting electrodes which are insulated from one to another. The charge on the electrodes is $+Q$ and $-Q$, and V represents the potential difference between the electrodes. Capacitance is measured in the SI unit of the Farad, $1F=1C/V$. The capacitance can be calculated if the geometry of the conductors and the dielectric properties of the insulator between the conductors are known. For example, the capacitance of a parallel plate capacitor constructed of two parallel plane electrodes of area A separated by a distance d is approximately equal to the following:

$$C = \varepsilon \frac{A}{d} \quad (2.2)$$

where C is the capacitance in farads, ε is the permittivity of the insulator used, A is the area of each plane electrode, measured in m^2 and d is the separation between the electrodes, measured in m . The equation 2.2 is a good approximation if d is small compared to the other dimensions of the electrodes. This is this geometry that we have used to measure the capacitance and thus the dielectric constant of our different samples (see chapter 5). The set-up used was a home-made sample holder consisting of four stainless steel coaxial wires on a stick. This set-up was made by Umut Adem and Agung Nugroho. The measurement were carried out using programs written using the software Labview. The different programs were written by Nandang Mufti. We used two kinds of capacitance bridges. For regular measurements, we used a PPMS (Physical Properties Measurement System) of Quantum Design model 6000 ($H_{max}=9T$; $\Delta T=1.8K-350K$) coupled to an Andeen-Hagerling 2500 capacitance bridge using a frequency of $1kHz$. For frequency dependence, we used an Agilent 4284A ($\Delta f=20Hz-1MHz$).

Pyroelectric current measurement

The pyroelectric effect, whereby a change in temperature in a material engenders a release of electric charge, has been known as a physically observable phenomenon for many centuries, being described by Theophrastus in 315 BC [3]. The effect occurs in any material which possesses a polar point symmetry. Thus, of the 32 possible group symmetries, there are 10 for which the materials possessing them are pyroelectric. These are, grouped according to crystal system and using International notation: triclinic (1), monoclinic (2, m), orthorhombic (2mm), tetragonal (4, 4mm), trigonal (3, 3m) and hexagonal (6, 6mm). Microscopically, the pyroelectric effect occurs because of the asymmetric environment experienced by electrically charged species within the crystal structure of the material. In materials the dipole moment can arise as a consequence of the packing in an ionic crystal, because of the alignment of polarized covalent bonds in molecular crystals or crystalline polymers or because of atomic displacements controlled by the position of hydrogen ions in a hydrogen bonded crystal.

Quantitatively, the pyroelectric effect is described in terms of a vector, the pyroelectric coefficient \vec{p} , given by the rate of change of \vec{P}_s with temperature (T). Thus:

$$\Delta \vec{P}_s = \vec{p} \Delta T \quad (2.3)$$

If a thin piece of pyroelectric is electroded as shown in figure 2.5, such that there is a component (p') of p perpendicular to the electroded surfaces (which have area A) then these charges can be detected as a current, i_p , flowing in an external circuit such that:

$$i_p = Ap'dT/dt \quad (2.4)$$

Usually, the geometry is chosen such that p is oriented perpendicular to the element electrodes, i.e. $p=p'$.

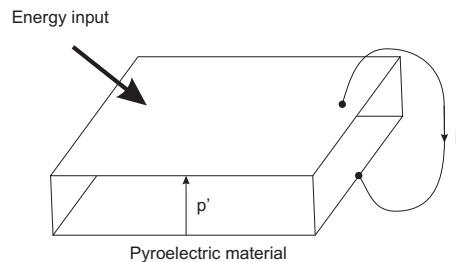


Figure 2.5: *Electroded pyroelectric element showing flow of pyroelectric current due to change in temperature.*

While a random assembly of crystals (polycrystalline/ceramic) cannot exhibit the polar symmetry necessary for pyroelectricity, the application of

an electrical field will re-orient the polar axes of the crystallites so that they have a component parallel to it, producing a net polarization. The size of the maximum \vec{P}_s which can be achieved for a random assembly of crystallites is simply related to the possible number of polar axes in the low symmetry phase which can be derived from the high symmetry phase. Thus after poling, \vec{P}_s would generally not reach the mono-domain bulk value.

From eqn 2.3 and 2.4, we can see that the determination of the polarization is done by integrating the changes of the current flowing through the material as function of temperature. This is how we effectively measure the polarization in our material (see chapter 5). For this purpose, we have used the same sample holder as previously described in figure 2.4. We measured the pyroelectric current using a electrometer Keithley 617. The poling process was done using a source unit Keithley 236 with $V_{max}=1100V$. The implementation for polarization measurement of the home-made set-up presented in figure 2.4 was done by Nandang Mufti.

2.2 Theoretical approach: Use of group-theory

The following section deals with symmetry arguments in the analysis of relevant materials. In the first part, we recall the main definitions, that one needs to know to do symmetry analysis. We illustrate the different definitions with the example of a group containing six elements which, as an abstract group we call \mathbf{G}_6^2 . In one of its realizations, this group is the symmetry group of an equilateral triangle. These group theoretical methods are used in the study of orbital ordering in RTiO_3 (see chapter 3). Further use of these tools/notions is done in the analysis of the mechanism leading to ferroelectricity in hexagonal RMnO_3 (see chapter 4). After extending the notions of group theory to magnetic space groups, we treat the case of the linear magnetoelectric effect. The use of magnetic symmetry is emphasized in chapters 5 and 6. The later chapter is presented to illustrate the importance of group theory as a powerful tool to identify new materials of importance.

2.2.1 Group theoretical techniques in magnetic structure analysis

General group theory concepts

We will first introduce notations/definitions in group theory which will be used later in this chapter and more generally in this thesis [4, 5].

Definition of a group:

A group \mathbf{G} is a set of elements together with a binary composition called a product such that:

- the product of any two elements in the group is defined and is a member of the group: if $A, B \in \mathbf{G}$ then $AB \in \mathbf{G}$
- the product is associative: $A(BC) = (AB)C$ for all $A, B, C \in \mathbf{G}$
- there exists a unique identity E in the group: $EA = AE = A$ for all $A \in \mathbf{G}$
- every element has a unique inverse element: given $A \in \mathbf{G}$ there exists a unique element A^{-1} such that $AA^{-1} = A^{-1}A = E$

From the definition of a group, it follows that a group is completely defined by its multiplication table. In fact, it is sufficient to give a set of relations involving certain elements from which the whole multiplication table can be constructed. The minimum set of elements allowing to generate the group is the set of generators. A set of generators is usually not unique. The user may choose the one which is the most handy for the purpose of a given study. In the International Tables of Crystallography [6], the crystallographic space groups are classified by their symbol. This symbol contains always a set of generators. However, sometimes it might not be the most convenient one. In the remaining part of this thesis, we will use both possibilities: the symbol or another set of generators.

| | | | | | |
|------------------|------------------|------------------|------------------|------------------|------------------|
| E | P | P ² | Q | PQ | P ² Q |
| P | P ² | E | PQ | P ² Q | Q |
| P ² | E | P | P ² Q | Q | PQ |
| Q | P ² Q | PQ | E | P ² | P |
| PQ | Q | P ² Q | P | E | P ² |
| P ² Q | PQ | Q | P ² | P | E |

Table 2.2: Multiplication table of the group \mathbf{G}_6^2 .

A geometrical realization of a group is the set of symmetry operations that carry an equilateral triangle, $\triangle ABC$, into itself. If the intersection of the medians of $\triangle ABC$ is denoted O then the operation P may be thought of as the 120° anticlockwise rotation about a line through O perpendicular to the plane ABC and Q may be thought of as the reflection in the line AO . Equally well we could have taken P to be a 120° clockwise rotation and Q to be the reflection in BO or for that matter in CO . In each case we would

obtain the same group but with its elements labelled differently. This is a simple example of the non-uniqueness of a set of generators.

Now, we will give several definitions which are necessary to introduce the notions of group representations.

Homomorphism and Isomorphism

Given 2 groups \mathbf{G} and \mathbf{G}' , a mapping θ of \mathbf{G} onto \mathbf{G}' which preserves multiplication is called a homomorphism. Thus for a homomorphism θ it follows that, for all $g_1, g_2 \in \mathbf{G}$,

$$(\theta g_1)(\theta g_2) = \theta(g_1 g_2) \quad (2.5)$$

If in addition θ is a one-to-one mapping, it is called an isomorphism: \mathbf{G} and \mathbf{G}' are then said to be isomorphic. If θ is an isomorphism and $\mathbf{G} = \mathbf{G}'$ then θ is called an automorphism.

Let $\mathbf{G} = \mathbf{G}_6^2$ and $\mathbf{G}' = \mathbf{G}_2^1$, the cyclic group of order 2 composed of elements E and P' with $P'^2 = E$ (E being the identity). Then if θ is defined so that $\theta E = E, \theta P = E, \theta P^2 = E, \theta Q = P'$, and $\theta(P^2 Q) = P'$, then θ is a homomorphism of \mathbf{G}_6^2 onto \mathbf{G}_2^1 . On the other hand, if it is given that θ is a homomorphism of \mathbf{G}_6^2 onto \mathbf{G}_2^1 then, by virtue of eqn. 2.5, it is sufficient in order to define θ to specify its action only on the generators of \mathbf{G}_6^2 .

Kernel

If $\theta \mathbf{G} = \mathbf{G}'$ is a homomorphism of \mathbf{G} onto \mathbf{G}' then the kernel of θ is the set of elements of \mathbf{G} that is mapped onto the identity of \mathbf{G}' .

For instance the kernel of the homomorphism θ defined in the previous example between the groups $\mathbf{G} = \mathbf{G}_6^2$ and $\mathbf{G}' = \mathbf{G}_2^1$ consists of the elements E, P and P^2 .

Subgroup

A subset \mathbf{H} of a group \mathbf{G} that is itself a group under the same binary composition as in \mathbf{G} is called a subgroup of \mathbf{G} .

The following are subgroups of \mathbf{G}_6^2 :

- \mathbf{G}_6^2 itself
- \mathbf{G}_3^1 , consisting of E, P and P^2
- \mathbf{G}_1^2 , consisting of E and Q
- $\mathbf{G}_1^{2'}$, consisting of E and PQ

- $\mathbf{G}_1^{2''}$, consisting of E and P^2Q
- \mathbf{G}_1^1 , consisting of the identity E alone

A group has always at least two subgroups, namely the group itself and the group consisting of the identity alone. Such subgroups are called improper subgroups. Other subgroups besides these two are called proper subgroups. Thus \mathbf{G}_6^2 has 4 proper subgroups.

Group Representations

Now that we have given several definitions about the abstract group theory, we need to introduce the tools that we will use in the remainder of this thesis. These tools are inclosed in what we call group representations. We will continue also here by illustrating when necessary using the case of the group \mathbf{G}_6^2 [4, 5].

Matrix group

A matrix group Δ is a group of non-singular (\equiv invertible) matrices. If all the matrices of the group are unitary then it is said to be an unitary matrix group. A unitary matrix is a $n \times n$ complex matrix U satisfying the condition $UU^* = U^*U = E$ where E is the identity matrix and U^* is the conjugate transpose (also called the Hermitian adjoint) of U . Note this condition says that a matrix U is unitary if and only if it has an inverse which is equal to its conjugate transpose U^* . In what follows we shall be concerned with matrix groups of finite order and with matrices of finite dimension.

Two matrices D_1 and D_2 are said to be conjugate if there exists a non-singular matrix S such that $D_1 = SD_2S^{-1}$. Two matrix groups Δ_1 and Δ_2 are said to be equivalent if there exists a non-singular matrix S such that $\Delta_1 = S\Delta_2S^{-1}$.

Every matrix group is equivalent to an unitary matrix group. The following symbols will be used in dealing with matrices:

- D^T for the transpose of D
- D^* for the complex conjugate of D
- $D^\dagger [= (D^*)^T]$ for the Hermitean conjugate of D
- $\tilde{D} [= (D^{-1})^T]$ for the contragredient of D

- $\dim D$ for the dimension of D

Trace-Character

The trace of a matrix D is the sum of its diagonal elements written $\text{Tr } D$. The character of a matrix group Δ is the function χ defined on all elements $D \in \Delta$ such that $\chi(D) = \text{Tr } D$.

Representation of a group

A representation of a group \mathbf{G} is a homomorphism γ of \mathbf{G} onto a group \mathbf{T} of non-singular linear operators acting on a finite-dimensional vector space \mathbf{V} over the complex field. We write $\gamma \mathbf{G} = \mathbf{T}_{\mathbf{G}}$, for all $g \in \mathbf{G}$.

From this definition, it follows that when γ is a representation then:

- $T_{g_1}(T_{g_2}\mathbf{x}) = T_{g_1g_2}\mathbf{x}$ for all $G_1, G_2 \in \mathbf{G}$ and for all $\mathbf{x} \in \mathbf{V}$
- $T_E\mathbf{x} = \mathbf{x}$ for all $\mathbf{x} \in \mathbf{V}$; that is, T_E is the identity operator
- $T_g^{-1}\mathbf{x} = T_{g^{-1}}\mathbf{x}$ for all $g \in \mathbf{G}$ and for all $\mathbf{x} \in \mathbf{V}$

If γ is an isomorphism the representation is said to be faithful.

Suppose now that we choose a basis $\langle \mathbf{x} |$ consisting of linearly independent vectors $\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_d$ spanning the space \mathbf{V} , and let us define matrices $\Gamma_{\mathbf{x}}(g)$ by the equations

$$T_g\mathbf{x}_i = \sum_{j=1}^d \mathbf{x}_j \Gamma_{\mathbf{x}}(g)_{ij} \quad (i = 1 \text{ to } d) \quad (2.6)$$

then $\Gamma_{\mathbf{x}}(g)$ is said to be the matrix representing G with respect to the basis $\langle \mathbf{x} |$ in the representation γ . The set of all distinct matrices $\Gamma_{\mathbf{x}}(G)$ is a matrix group and it is the homomorphic image of \mathbf{G} under the mapping $G \rightarrow \Gamma_{\mathbf{x}}(G)$, the kernel of the homomorphism being the elements of \mathbf{G} mapped onto the unit matrix.

Let \mathbf{G} be the group \mathbf{G}_6^2 , the multiplication table of which is given in table 2.2. A geometrical realization of this group was described in the previous illustration. This involved an equilateral triangle ABC with centroid O . Let $\overrightarrow{OA} = \vec{a}$, $\overrightarrow{OB} = \vec{b}$ and $\overrightarrow{OC} = \vec{c}$; then $\vec{a} + \vec{b} + \vec{c} = \vec{0}$, and the plane of the triangle forms a vector space \mathbf{V} of dimension 2. This, we take to be the underlying vector space of the representation γ . Take as basis for this vector space $\vec{x}_1 = \vec{b}$ and $\vec{x}_2 = \vec{c}$. The representation γ maps P and Q onto elements T_P and T_Q which are respectively an anti-clockwise rotation of 120° about O and a reflection in the line AO . The operators T_P and T_Q

are operators acting on \mathbf{V} and from their definition $T_P \vec{b} = \vec{c}$, $T_P \vec{c} = \vec{a} = -\vec{b} - \vec{c}$, $T_Q \vec{b} = \vec{c}$ and $T_Q \vec{c} = \vec{b}$. From eqn. 2.6 it follows that

$$\Gamma_{\mathbf{x}}(\mathbf{P}) = \begin{pmatrix} 0 & -1 \\ 1 & -1 \end{pmatrix} \quad \text{and} \quad \Gamma_{\mathbf{x}}(\mathbf{Q}) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad (2.7)$$

Since γ is a homomorphism the rest of the matrix group follows from multiplication. Thus, for example,

$$\Gamma_{\mathbf{x}}(\mathbf{P}^2) = \Gamma_{\mathbf{x}}(\mathbf{P})\Gamma_{\mathbf{x}}(\mathbf{P}) = \begin{pmatrix} -1 & 1 \\ -1 & 0 \end{pmatrix} \quad (2.8)$$

and so on. It can easily be checked that γ is a faithful representation. However it contains non-unitary matrices. γ is of dimension 2. Thus if χ_γ is the character of γ it follows that $\chi_\gamma(\mathbf{E})=2$, $\chi_\gamma(\mathbf{P})=\chi_\gamma(\mathbf{P}^2)=-1$ and $\chi_\gamma(\mathbf{Q})=\chi_\gamma(\mathbf{PQ})=\chi_\gamma(\mathbf{P}^2\mathbf{Q})=0$.

Let $\langle \mathbf{x} \rangle$ and $\langle \mathbf{y} \rangle$ be two bases of \mathbf{V} defined so that

$$\mathbf{y}_k = \sum_{i=1}^d \mathbf{x}_i S_{ik} \quad (k = 1 \text{ to } d) \quad (2.9)$$

where S is non-singular, then

$$\Gamma_{\mathbf{y}}(\mathbf{G}) = S^{-1}\Gamma_{\mathbf{x}}(\mathbf{G})S \quad \text{for all } G \in \mathbf{G}. \quad (2.10)$$

That is to say, a change of basis leads to matrix groups $\Gamma_{\mathbf{x}}(\mathbf{G})$ and $\Gamma_{\mathbf{y}}(\mathbf{G})$, which are equivalent. Hence, it is possible to choose a basis $\langle \mathbf{z} \rangle$ in \mathbf{V} such that $\Gamma_{\mathbf{z}}(\mathbf{G})$ is a unitary matrix group.

Irreducible Representation

Let γ be a representation of \mathbf{G} so that $\mathbf{T}=\gamma\mathbf{G}$ is a group of non-singular linear operators acting on a vector space \mathbf{V} . \mathbf{U} is said to be an invariant subspace of \mathbf{V} under \mathbf{T} if

- \mathbf{U} is a vector subspace of \mathbf{V}
- $T_G \mathbf{x} \in \mathbf{U}$ for all $T_G \in \mathbf{T}$ and all $\mathbf{x} \in \mathbf{U}$

If \mathbf{V} has no proper invariant subspace under \mathbf{T} (that is, no subspace invariant under \mathbf{T} except \mathbf{V} itself and the zero-vector) then γ is said to be an irreducible representation. If there exists a proper invariant subspace under \mathbf{T} then γ is said to be reducible. If \mathbf{V} can be split up into the direct sum of subspaces each of which is invariant under \mathbf{T} and each of which is the carrier space for an irreducible representation of \mathbf{G} then γ is said to be completely reducible.

There are a number of properties for irreducibility which are useful. In many quantum mechanical applications each irreducible representation will display the transformations properties of a set of degenerate eigenfunctions. Thus, they are preferable than the reducible representations. A representation is irreducible if, and only if, the only matrices which commute with all matrices of the representation are scalar multiples of the unit matrix. Moreover, let \mathbf{G} be a group of order $|\mathbf{G}|$ with elements $g_1, g_2, \dots, g_{|\mathbf{G}|}$. Then $\Gamma(\mathbf{G})$ is an irreducible representation if and only if

$$\frac{1}{|\mathbf{G}|} \sum_{i=1}^{|\mathbf{G}|} |\chi_{\gamma}(G_i)|^2 = 1 \quad (2.11)$$

Another important result from the above properties is the decomposition of a representation in irreducible representations. Let Γ be an arbitrary matrix representation of \mathbf{G} with character χ then when Γ has been completely reduced by suitable equivalence transformations to block-diagonal form it becomes a direct sum of irreducible representations $\sum_{i=1}^r c_i \Gamma^i$, where

$$c_i = \frac{1}{|\mathbf{G}|} \sum_{i=1}^r r_i \chi(C_i) \chi^{i*}(C_i) \quad (2.12)$$

Subduced representations:

We shall give here the definition of a subduced representation. It is of prime importance in the study of a phase transition. It is on this principle that we have based part of our analysis for hexagonal RMnO_3 (see chapter 4).

Let Γ be an irreducible representation of \mathbf{G} , character $\chi^{\Gamma}(g)$; then the number of times that Γ appears in the decomposition of $\Gamma^j \uparrow \mathbf{G}$ into irreducible representations of \mathbf{G} is equal to the number of times the irreducible representation Γ^j appears in $\Gamma \downarrow \mathbf{H}$, where \mathbf{H} is a subgroup of \mathbf{G} . Here $\Gamma \downarrow \mathbf{H}$ denotes the restriction of Γ to elements of \mathbf{H} and is commonly called the representation of \mathbf{H} subduced by Γ ; since \mathbf{H} is a subgroup of \mathbf{G} it is clear that $\Gamma \downarrow \mathbf{H}$ is a representation of \mathbf{H} of the same dimension as Γ . $\Gamma^j \uparrow \mathbf{G}$ is called the induced representation of Γ^j in \mathbf{G} .

Magnetic symmetries

Antielements: Polar versus Axial vectors

We discuss in this part the main features of the representation analysis of magnetic structures [5]. We should keep in mind that the spins are axial vectors or pseudovectors. This means that they transform like a (polar) vector under rotations but are invariant under spatial inversion. This is not

the case for polar vectors (e.g. the polarization) which are not invariant under spatial inversion. The mathematical expression of the time inversion operator is defined by $R^2=E$, where E is the identity operator. The difference between a spin (axial vector) and a polarization for instance (polar vector) is that a symmetry element acts on the current loop which generates the spin. We illustrate this statement in figure 2.6 where we look at the action of an inversion center on a current loop.

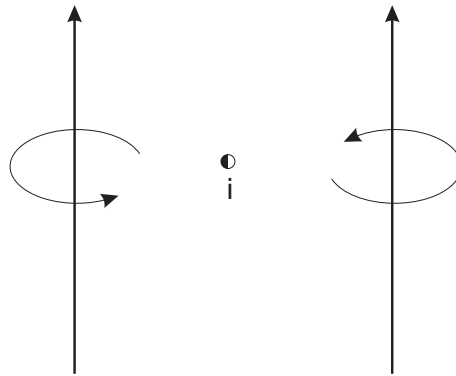


Figure 2.6: *Effect of the inversion center i on a current loop generating a spin*

We can see that contrary to a polar vector (e.g. polarization), the direction of the spin is not reversed under the inversion center. In figure 2.6, we see that we have a ferromagnetic coupling between the two spins. Consequently, for an antiferromagnetic coupling the inversion center will be broken. In order to describe properly the special properties of the spins, we need to define new symmetry elements. Historically, they have been introduced as new symmetry operators (so-called antielements) which are the product of the conventional symmetry elements g with the time inversion operator R . These new operators are denoted with a prime with respect to the conventional operators.

$$g' = gR = Rg \quad \text{with} \quad R^2 = E \quad (2.13)$$

These new symmetry elements enlarge the number of possible groups from the conventional 230 space groups from the International Tables of Crystallography [6]. Indeed, there are 32 crystalline classes which yield to 90 magnetic classes including the paramagnetic ones (which are in fact the above 32). These 90 magnetic classes give rise to 1651 magnetic space groups. These 1651 magnetic space groups contain also the paramagnetic space groups, which are the known 230 space groups from the International Tables of Crystallography [6]. They will be usually denoted e.g. $Pnma1'$ for the paramagnetic phase of a compound crystallizing in the space group $Pnma$.

The magnetic symmetry of a crystal coincides with the group of symmetry operations which leave invariant the mean density of electric current invariant. This group can be obtained by combining the rotations, reflections and translations forming the crystallographic group \mathbf{G} of the crystal, with the time-reversal operator R . They are mainly 3 kinds of magnetic groups:

- "Black and white" magnetic groups \mathbf{M} resulting from the combination of R with half of the symmetry operations of the ordinary point group \mathbf{G} . Such groups can be written:
 $\mathbf{M}=\mathbf{H}+(\mathbf{G}-\mathbf{H})R$
- "White" groups which also describe a magnetic structure:
 $\mathbf{M}=\mathbf{G}$
- "Grey groups" labelled $\mathbf{G}1'$ which contain the operations of \mathbf{G} plus their combination with R :
 $\mathbf{M}=\mathbf{G}+R\mathbf{G}$

We note that $RE=R$ is by itself a symmetry operation of the group \mathbf{G}' . Thus, these groups describe a paramagnetic structure. Black and White groups and also White groups describe either an antiferromagnetic or ferromagnetic structures.

Star and little group $\mathbf{G}_{\vec{k}}$ of \vec{k}

In most of the transitions between a high temperature phase \mathbf{G} and a low temperature phase \mathbf{H} , one of the modes of \mathbf{G} will become soft (its frequency goes to zero at T_C). This mode is characterized by a wave-vector \vec{k} . One can define the little-group of \vec{k} denoted $\mathbf{G}_{\vec{k}}$. The little-group of $\mathbf{G}_{\vec{k}}$ is the set of symmetry elements which leave invariant the wave-vector \vec{k} . If g is a symmetry element of \mathbf{G} , \vec{k} is said to be invariant by g if $g\vec{k} - \vec{k} = 0$ or \vec{n} , \vec{n} being a translation of the lattice.

One can define the star of \vec{k} . It is the set of inequivalent vectors \vec{k} which are generated by the application of all the elements g of \mathbf{G} . Each \vec{k} is an arm of the star. The number of arms in the star of \vec{k} is equal to the index of the subgroup $\mathbf{G}_{\vec{k}}$ with respect to the group \mathbf{G} .

Axial and permutation representations

The effect of symmetry element is two-fold: it will act to change the position of an atom, and reorientate the magnetic moment, e.g. atom 1 moves to the position of atom 2, and its moment is reversed. The combination of

these two results are described by the magnetic representation, Γ . We will examine these two effects separately.

A symmetry operator $g=\{h|\tau\}$ acts on both the position r_j of the atom and on the components α of the axial vector that describes the moment. h is the rotational part of the symmetry element and τ the translational part (Seitz notation). The operation that sends r_j in the zeroth cell to r_i in the p th cell can be symbolically stated as:

$$g(j0) \longrightarrow (ia_p) \quad (2.14)$$

In other terms, the effect of a symmetry operation g is to permute the column matrix of atom labels, \mathbf{P} :

$$g(\mathbf{P}) \longrightarrow \mathbf{P}' \quad (2.15)$$

This operation is governed by a permutation representation, Γ_{perm} , which has matrices of order N_A , where N_A is the number of equivalent positions of the crystallographic site. It is important to note that when a symmetry operation results in an atomic position that is outside the zeroth cell, a phase factor must be included that relates the generated position to that in the zeroth cell. This phase is simply given by:

$$\theta = -2\pi\mathbf{k}\cdot\mathbf{T} \quad (2.16)$$

where \mathbf{T} is the translation vector, that relates the original and generated atoms.

The second effect of this symmetry operation is to transform the spin components with index α , ($\alpha=x,y,z$) of the reference spin j into the index α' of the atom r_i . These transformations are described by the axial vector representation, \tilde{V} , the character of which is given by:

$$\chi_{\tilde{V}}^h = \sum_{a=b} R_{ab}^h \det(h) \quad (2.17)$$

where R_{ab}^h refers to a specific element a,b of the rotation matrix h , and $\det(h)$ represents the determinant of the rotation matrix R^h , and has the value of +1 for a proper and -1 for an improper rotation.

The magnetic representation Γ describes both the result of the symmetry operation on the atomic positions, and on the axial vectors that describe the magnetic moment. As these effects are independent, the magnetic representation is given by their direct product:

$$\Gamma = \tilde{V} \times \Gamma_{perm} \quad (2.18)$$

Or, in terms of the matrices for the representations themselves

$$D_{h,\tau_h}^\Gamma = D_h^{\tilde{V}} \times D_{h,\tau_h}^{\Gamma_{perm}} \quad (2.19)$$

The Γ representation of eqn. 2.18 is usually reducible. To reduce this representation, we have to use the formula of eqn. 2.12.

Remark: Whereas for a unitary group there are representations and irreducible representations, for a non-unitary group in which half the elements are unitary and the other half are anti-unitary, there are corepresentations and irreducible corepresentations. Grey and Black and White magnetic groups contain both unitary and anti-unitary operations. One has then to consider the problem of the representations containing anti-unitary elements. If we write a anti-unitary group $\mathbf{M} = \mathbf{G} + \mathbf{R}\mathbf{G}$ as for the grey paramagnetic groups, where g_i are the elements of \mathbf{G} and $a_i = \mathbf{R}g_i$. If $D(g_i)$ and $D(a_i)$ are the matrices associated with the g_i and a_i respectively, it is not possible to construct matrix representations of \mathbf{M} following the usual composition rule for representations of unitary groups: $D(h_i)D(h_j) = D(h_i h_j)$, but one can form a corepresentation of \mathbf{M} using the alternative composition rules:

$$\begin{aligned} D(g_i)D(g_j) &= D(g_i g_j) \\ D(g_i)D(a_j) &= D(g_i a_j) \\ D(a_i)D^*(a_j) &= D(a_i g_j) \\ D(a_i)D^*(a_j) &= D(a_i a_j) \end{aligned} \quad (2.20)$$

It has been shown that the irreducible corepresentations of a magnetic non-unitary group \mathbf{M} , can be deduced from the irreducible representations of the associated crystallographic subgroup \mathbf{G} [7]. Three situations are distinguished depending if the matrices of the considered irreducible representations are real or imaginary, and also on the nature of the anti-unitary operations pertaining to \mathbf{M} . If we only consider here the question of essential interest in the interpretation of magnetically ordered systems, namely the description of transitions from a paramagnetic to a magnetically ordered phase, then we can restrict ourselves to the problem of constructing the irreducible corepresentations of paramagnetic groups. As the time reversal operator \mathbf{R} belongs by itself to the grey groups, it is possible to show that no degeneracies take place for the energy eigenvalues of the Hamiltonian of the system. So the representation space has the same dimensionality for the irreducible corepresentations and for the corresponding irreducible representations.

Determination of primed and unprimed elements

In order to determine the magnetic space group and also its magnetic point group, one needs to know when a symmetry element should be primed or not. In other words, when the current loop is invariant: by application of a symmetry element or by its corresponding antielement?

We will illustrate this point by taking the example of the point group 222 (D_2 , table 2.3).

| | 1 | 2_z | 2_y | 2_x | Magnetic point group |
|-------|---|-------|-------|-------|----------------------|
| A | 1 | 1 | 1 | 1 | 222 |
| B_1 | 1 | 1 | -1 | -1 | $2'2'2'$ |
| B_2 | 1 | -1 | 1 | -1 | $2'2'2'$ |
| B_3 | 1 | -1 | -1 | 1 | $2'2'2'$ |

Table 2.3: Irreducible representations for point group D_2 .

Each line in table 2.3 corresponds to an irreducible representation (IR). To each IR, we can associate a magnetic point group by keeping the same elements when the character is +1 and changing them to antielements when the character is -1 (in the case of real values). For the case of complex values, there always exists a unitary transformation which can transform the elements of IRs to real values.

We will consider here and in the remainder of the thesis only the cases where the magnetic structure is commensurate with the lattice. The corresponding magnetic point groups are given in the last column of table 2.3. Mathematically, it means that we have two possibilities. If g sends atom 1 on atom 2 thus:

$$\tilde{V}(g)S_1 = -S_2 \quad or \quad +S_2$$

If one obtains $-S_2$, g has to be primed otherwise not. In the investigation for magnetic symmetry determination, there is in fact another possibility: $\tilde{V}(g)S_1 \neq -S_2 \quad or \quad \neq +S_2$. In that case, it means that the symmetry element g is lost in the magnetically ordered phase.

2.2.2 The magnetoelectric effect

Compounds presenting coexistence of several possible ferroic states have attracted a lot of attention since several decades due their interesting properties. Among them, materials presenting simultaneously ferroelectric and magnetic orders were the subject of intensive studies in recent years [8]. They have interesting properties allowing the manipulation of electric and magnetic moments by magnetic and electric fields, respectively. We refer to multiferroics, as compounds presenting ferroelectric order and anti or

ferromagnetic order. The d^0 configuration that is favored for typical ferroelectrics as BaTiO_3 is incompatible with magnetism. This feature explains the interest generated by these compounds.

However there is another way to generate polarization which is through the magnetoelectric effect. This effect has been first predicted by Curie in 1894 [9]. He stated that materials that develop an electric polarization in a magnetic field or a magnetization in an electric field may exist. Later, based on the prediction of Dzyaloshinskii [10], Astrov showed the existence of magnetoelectric effect in Cr_2O_3 [11]. The general expression for the free-energy of such materials (we will consider here only the linear effect) can be written in the form:

$$\Phi = \Phi_0 - \alpha_{ij} E_i H_j \quad (2.21)$$

α_{ij} refers to the components of the magnetoelectric tensor. If an electric field \mathbf{E} is applied to a crystal with potential 2.21, a magnetization will be produced:

$$M_j = -\frac{\partial \Phi}{\partial H_j} = \alpha_{ij} E_i \quad (2.22)$$

And the conjugate expression, one can produce polarization while applying a magnetic field:

$$P_i = -\frac{\partial \Phi}{\partial E_i} = \alpha_{ij} H_j \quad (2.23)$$

Experimentally, since most of the research for new magnetoelectrics is concentrated on bulk, this is often how is evidenced the magnetoelectric coupling in these materials. Indeed since, the electric field necessary to polarize the bulk is usually beyond the reachable value of the experimental set-ups. While a lot of effort has been put into the search and design of new magnetoelectric compounds, there is no systematic approach to look for new materials. However, from the equations 2.22 and 2.23, a systematic symmetry approach seems to be sufficient in the search for new materials. Historically, it has been this approach which has been privileged. However at the revival of the research on multiferroic/magnetoelectric compounds, this approach has been more or less forgotten.

\mathbf{M} like \mathbf{H} is an axial vector and \mathbf{P} like \mathbf{E} is a polar vector. As a consequence of the equations 2.22 and 2.23 (one can express \mathbf{P} function of \mathbf{H} and \mathbf{M} function of \mathbf{E}), a linear magnetoelectric effect will be allowed under the application of a magnetic field when terms like $L_i M_j P_k$ or $M_i M_j P_k$ are allowed in the free-energy of the system. In these terms, L_i is an antiferromagnetic component and M_j a ferromagnetic component. Indeed if one looks at the minima of the free-energy (eq. 2.22 and 2.23), one can replace \mathbf{E} as a function of \mathbf{M} and \mathbf{H} as a function of \mathbf{P} . However, due to

the time inversion which reverse the sign of the spins, terms like $L_i P_k$ or $M_j P_k$ won't be invariant. Consequently, if the free energy of the system contains terms like $L_i M_j P_k$ or $M_i M_j P_k$, the system will be able to present a linear magnetoelectric effect (chapter 6). Later on, we will either derive the full free-energy of the system by considering the terms which are allowed by symmetry, either just look for terms like above to predict a possible linear magnetoelectric effect. We present our results and give examples of predicted magnetoelectric materials using systematic symmetry investigation (chapter 6).

In the remainder of this chapter, we will discuss only the linear magnetoelectric effect since it is the one presenting the most promising for applications and the easier to probe experimentally. While speaking about the existence of magnetization, it is obvious that the magnetoelectric effect is forbidden in all dia and paramagnetic compounds. In terms of symmetry, it means that the symmetry of these compounds possess R (the time inversion element) which causes the reversal of the magnetic moment density. The magnetoelectric effect is also forbidden if the magnetic space group contains translations multiplied by R because in these cases the point group also possesses R as a separate element which is equivalent to a dia or paramagnetic group. We remind the reader that the vector \mathbf{H} is an axial vector while the \mathbf{E} vector is a polar vector and in consequence they behave differently under R . There are in total 122 magnetic point groups which describe 1651 magnetic space groups. These numbers may look very big if one wants to do a systematic approach. However, we will see that in several magnetic space groups, the situation regarding the eventual presence of magnetoelectricity is simplified a lot.

From eqn. 2.21, we can see that α_{ij} is a tensor of second rank and its components change sign under the application of R . The magnetic centrosymmetric space groups do not allow a magnetoelectric effect. However the ones which possess the element $\bar{1}'$ resulting from the application of spatial inversion and time inversion can present a magnetoelectric effect. If one does a systematic analysis of the 122 magnetic point groups, one can see that the magnetoelectric effect is allowed only in 58 magnetic point groups. Among these ones, there are only 11 possible forms for the tensor α_{ij} . The general expression of the magnetoelectric tensor is [12]:

$$\begin{pmatrix} \alpha_{11} & \alpha_{12} & \alpha_{13} \\ \alpha_{21} & \alpha_{22} & \alpha_{23} \\ \alpha_{31} & \alpha_{32} & \alpha_{33} \end{pmatrix} \quad (2.24)$$

The different forms of the tensor α_{ij} are presented in table 2.4 [12].

| Magnetic crystal classes | Non zero tensor components α_{ij} |
|--|---|
| 1 and $\bar{1}$ ' | α_{ij} for $(i,j) \in [1,2,3]$ |
| 2, m' and $2/m'$ | $\alpha_{11}, \alpha_{13}, \alpha_{22}, \alpha_{31}, \alpha_{33}$ |
| m , $2'$ and $2'/m$ | $\alpha_{12}, \alpha_{21}, \alpha_{23}, \alpha_{32}$ |
| 222, $m'm'2$ and $m'm'm'$ | $\alpha_{11}, \alpha_{22}, \alpha_{33}$ |
| $mm2$, $2'2'2$, $2'mm'$ and mmm' | α_{12}, α_{21} |
| 4 , $\bar{4}'$, $4/m'$, 3 , $\bar{3}'$, 6 , $\bar{6}'$ $6/m'$ | $\alpha_{11}=\alpha_{22}, \alpha_{12}=-\alpha_{21}, \alpha_{33}$ |
| $\bar{4}$, $4'$, $4'/m'$ | $\alpha_{11}=\alpha_{22}, \alpha_{12}=-\alpha_{21}$ |
| 422 , $4m'm'$, $4'2m'$, $4/m'm'm'$, 32 , $3m'$, $\bar{3}'m'$, 622 , $6m'm'$, $\bar{6}'m'2$, $6/m'm'm'$ | $\alpha_{11}=\alpha_{22}, \alpha_{33}$ |
| $42'2'$, $4mm$, $\bar{4}'2'm$, $4/m'mm$, $32'$, $3m$, $\bar{3}'m$, $62'2'$, $6mm$, $\bar{6}'m2'$, $6/m'mm$ | $\alpha_{12}=-\alpha_{21}$ |
| $4'22'$, $4'm'm$, $\bar{4}2m$, $4'/m'm'm$, $\bar{4}2'm'$ | $\alpha_{11}=-\alpha_{22}$ |
| 23 , $m'\bar{3}'$, 432 , $\bar{4}'3m'$, $m'\bar{3}'m'$ | $\alpha_{11}=\alpha_{22}=\alpha_{33}$ |

Table 2.4: Expressions of the tensor α_{ij} in the case of the linear magnetoelectric effect [12].

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