

General introduction to representation theory

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1 Introduction

Molecules and crystals are usually symmetric objects, i.e. the spatial disposition of atoms are left invariants by a number of symmetry transformations. Their physical properties, described by tensors, have also a certain degree of symmetry, governed by the specific transformation of the tensorial quantity under symmetry operations of the body. The collection of symmetry operations, generated by symmetry elements of the molecule or crystal, has the structure of a group in the mathematical sense. One can therefore apply the powerful mathematical tools developed in group theory, to the study of physical properties of solids. To be more precise, physics uses part of group theory known as the theory of representations.

The purpose of representation theory is to study how the symmetry group of the molecule/crystal act on the vector space formed by the physical quantity relevant to the problem. Symmetrical elements of the space can be created and classified according to their symmetry. Representation theory is used for example by spectroscopists to classify vibration modes of a molecule/crystal and determine selection rules. It is used to determine crystal field schemes and to construct molecular orbitals (LCAO) in transition metal complexes. Of course, and this is entirely what this workshop is about, representation theory is a *essential* tool to study the arrangement of magnetic moments in an ordered state. The role of this lecture is to give an introduction to the practical use of group theory and to familiarize the audience with concepts and notations that will be used in the rest of the workshop. I have decided to use concrete examples throughout the lecture to highlight the most important points of the theory. This lecture is intended for beginners in the field, with the aim to provide enough background in group theory and crystallography for more specialized lectures. The discussion will be restricted to finite groups, with mainly applications at a molecular level where only point group symmetry is considered. The theorems will be given without proofs, and the reader may want to refer to a number of textbooks listed in the bibliography section for a more complete treatment.

2 Point group symmetry

2.1 Symmetry operations in molecules

Molecules are *finite* objects with usually a certain degree of symmetry, i.e. there are a number of symmetry elements in the body, such as points, lines or planes from which symmetry operations can be carried out and leave the molecule invariant. Let's take the water molecule for example as shown in figure 1. The molecule is left invariant by a 180 ° rotation along the z-axis. It is also left invariant by mirror operations in the xz and yz planes, respectively.

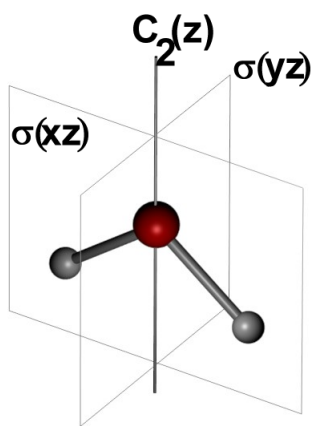


Figure 1: Symmetry elements of the water molecule.

In molecules, the combination of three type of symmetry elements (point, lines, planes) give rise to four kinds of symmetry operations, as explained below. We will note that two notations are used to label the symmetry operations, and, as we will discuss later, point groups. One, the so-called Schoenflies notation, is usually preferred by spectroscopists while the other, the Hermann-Mauguin notation is used in crystallography. I will use systematically both notations when discussing point group properties.

The four kinds of symmetry operations in molecules:

1) Inversion The symbol for the inversion operation is i in Schoenflies notation and $\bar{1}$ in Hermann-Mauguin notation. An inversion center changes the coordinates of each atom (x,y,z) in the molecule to $(-x,-y,-z)$.

2) Reflections The symbol for reflections through planes is σ in Schoenflies notation and m in Hermann-Mauguin notation.

3) Proper rotations The symbol for proper rotation axis of order n is C_n

in Schoenflies notation and n in Hermann-Mauguin notation. A rotation axis of order n generates rotation operation of $2\pi k/n$ with $k=1,\dots,n$. Each of these operations is noted C_n^k in Schoenflies notation. The convention for proper and improper rotations is anti-clockwise.

4) Improper rotations The symbol for improper axis of order n , is S_n in Schoenflies notation and \bar{n} in Hermann-Mauguin notation. An improper rotation operation of order n corresponds to the successive rotation operation (of order n) and reflection through a plane perpendicular to the rotation axis. This operation can exist on its own, i.e. does not require the existence of a proper rotation axis and a perpendicular mirror plane. For example in tetrahedral geometry, as seen on figure 2, the S_4^1 operation generated from the S_4 improper axis, transform point 1 into point 3, or point 2 into point 4. However, neither a proper 4-fold rotation axis, nor a mirror plane perpendicular to it are symmetry elements.

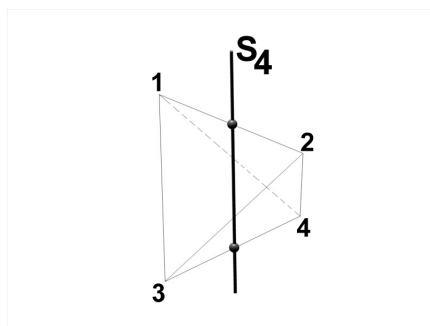


Figure 2: Improper 4-fold axis in a tetrahedron

2.2 Symmetry groups in molecules

By studying the geometry of a given body, here molecules, one can find a collection of symmetry operations that leave the body globally invariant. This collection of symmetry operations possesses a very basic but essential property, since it forms a group in the mathematical sense. I would like to note that this collection of operations can be infinite in some cases, for example for a linear molecule where rotations of any angle along the axis leaves the body invariant. However, in the rest of the document, one will encounter only finite groups. Let recall the generic definition of a group and verify that the symmetry operations that leave the water molecule invariant, together with the identity operation (labelled E or 1 in), has the structure of a group:

Definition of a group:

1) Is is a collection of elements for which an associative law of combination is defined and such that for any pair of elements g and

h , the product gh is also element of the collection

- 2) It contains a unitary element, E , such that $gE=g$
- 3) Every element g has an inverse, noted g^{-1} such that $gg^{-1}=E$.

We can verify that the symmetry operations of the water molecule has indeed the structure of a group by constructing what is known as the *multiplication table* of the group, reported in table I. This is a table, where the elements (here the symmetry operations) displayed horizontally and vertically are combined and their product reported in the corresponding table entry. The order in which the symmetry operations are applied is important since the law of combination is non necessarily commutative. We will note symbolically the combination (or product) of two operations g and h , gh . In this convention, the operation h is carried out first and g second. We can verify on the previous example that the group property is verified, i.e. the product of two symmetry operations is always element of the group, and that each element possesses an inverse. In this particular case, one also remark than the group is also commutative, since for each element g and h , $gh=hg$. We will see later on that commutative groups, named *Abelian* groups, have interesting additional properties.

Order of a group : The order of a group is its cardinality, i.e. its number of elements.

	E	$C_2(z)$	$\sigma(xz)$	$\sigma(yz)$
E	E	$C_2(z)$	$\sigma(xz)$	$\sigma(yz)$
$C_2(z)$	$C_2(z)$	E	$\sigma(yz)$	$\sigma(xz)$
$\sigma(xz)$	$\sigma(xz)$	$\sigma(yz)$	E	$C_2(z)$
$\sigma(yz)$	$\sigma(yz)$	$\sigma(xz)$	$C_2(z)$	E

Table 1: Multiplication table of the point group C_{2v}

2.3 Classes of symmetry operations

Before we go further, one needs to explain the important concept of classes and for that, to define the term *similarity transformation*. If g and x are elements of a group, then the element h such that

$$h = x^{-1}gx \tag{1}$$

is know as the similarity transform of g by x . We also say that g and h are conjugate.

In a group structure, a set of elements which are all conjugate to one another is called a class.. Basically, a class represents a set of operations that have the same geometrical properties, and are therefore regrouped. The similarity transformation expresses the fact that a given operation g is equivalent to another operation h in a different coordinate system, that can be accessed by an operation of the group.

Let's try to find similarity transformations in the group of water molecule. By using the multiplication table, one can easily see that each element of the group is only conjugate to itself (this property is of course always verified). For example, the similarity transformations of the $C_2(z)$ operation gives:

$$\sigma(xz)^{-1}C_2(z)\sigma(xz) = \sigma(xz)C_2(z)\sigma(xz) = \sigma(xz)\sigma(yz) = C_2(z) \quad (2)$$

$$\sigma(yz)^{-1}C_2(z)\sigma(yz) = \sigma(yz)C_2(z)\sigma(yz) = \sigma(yz)\sigma(xz) = C_2(z) \quad (3)$$

Therefore, the group of the water molecule has 4 operations, arranged into 4 classes.

If we take a molecule with a different geometry, say NH_3 represented in figure 3, we can find similarity transformations between elements of the group. Let's identify the symmetry elements. One finds a 3-fold axis and 3 vertical mirror planes, that we will label $\sigma_v(1)$, $\sigma_v(2)$ and $\sigma_v(3)$. The symmetry operations are E , C_3^1 , C_3^2 , $\sigma_v(1)$, $\sigma_v(2)$ and $\sigma_v(3)$. With the help of the multiplication table (table 2), one can easily find that there are 3 classes of operations in the symmetry group of the NH_3 molecule, E , (C_3^1, C_3^2) and $(\sigma_{v1}, \sigma_{v2}, \sigma_{v3})$. For example:

$$\sigma_{v1}^{-1}C_3^1\sigma_{v1} = \sigma_{v1}\sigma_{v2} = C_3^2 \quad (4)$$

$$(C_3^1)^{-1}\sigma_{v1}C_3^1 = C_3^2\sigma_{v3} = \sigma_{v2} \quad (5)$$

$$(C_3^2)^{-1}\sigma_{v1}C_3^2 = C_3^1\sigma_{v2} = \sigma_{v3} \quad (6)$$

Since symmetry operations belonging to the same class are "equivalents", one usually doesn't list all symmetry elements but rather the different classes, preceded by the number of operations in the class. For example, for the group of the NH_3 molecule, we will list E , $2C_3$, $3\sigma_v$.

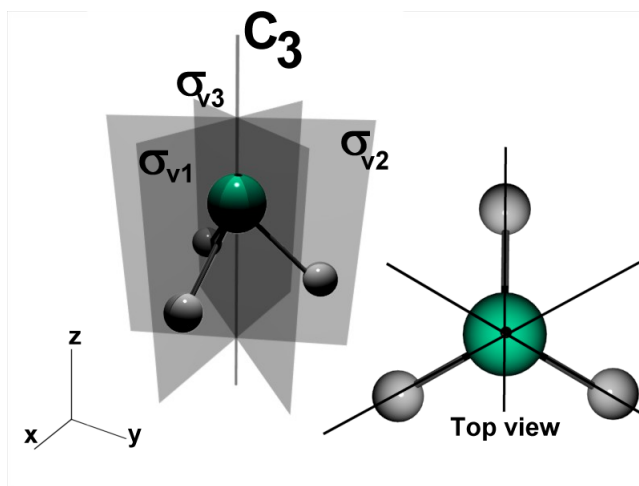


Figure 3: Symmetry elements in the NH_3 molecule

C_{3v}	E	C_3^1	C_3^2	σ_{v1}	σ_{v2}	σ_{v3}
E	E	C_3^1	C_3^2	σ_{v1}	σ_{v2}	σ_{v3}
C_3^1	C_3^1	C_3^2	E	σ_{v2}	σ_{v3}	σ_{v1}
C_3^2	C_3^2	E	C_3^1	σ_{v3}	σ_{v1}	σ_{v2}
σ_{v1}	σ_{v1}	σ_{v3}	σ_{v2}	E	C_3^2	C_3^1
σ_{v2}	σ_{v2}	σ_{v1}	σ_{v3}	C_3^1	E	C_3^2
σ_{v3}	σ_{v3}	σ_{v2}	σ_{v1}	C_3^2	C_3^1	E

Table 2: Multiplication table of the point group C_{3v}

2.4 Point groups

The collection of symmetry operations possessed by a molecule is named a *Point Group* (at least one point is invariant by all symmetry operations). The different point groups are obtained by combining a number of symmetry elements - inversion center, proper and improper rotations-axis, mirror planes-. There is limited number of such points groups which are labeled using two different notations. Chemists usually prefer the Schoenflies notation whereas crystallographers use the Hermann-Mauguin notation. In most cases, it is straightforward to find the point group of a given molecule by using a systematic procedure as illustrated in the flow chart of figure 4 (Cotton). It is important to note that molecules can be invariant by rotation of order 5,7,... For crystals, where translational periodicity is required, only point groups obtained by combining the inversion center, mirror planes and (proper and improper) **rotation axis of order 2,3,4,6** are valid. There are 32 crystallographic point groups (listed in table 3) which, combined with translations, give rise to 230 space groups.

nonaxial	$C_i(\bar{1}), C_s(m)$
cyclic	$C_1(1), C_2(2), C_3(3), C_4(4), C_6(6)$
cyclic with horizontal planes	$C_{2h}(2/m), C_{3h}(3/m), C_{4h}(4/m), C_{6h}(6/m)$
cyclic with vertical planes	$C_{2v}(mm2), C_{3v}(3m), C_{4v}(4mm), C_{6v}(6mm)$
dihedral	$D_2(222), D_3(32), D_4(422), D_6(622)$
dihedral with horizontal planes	$D_{2h}(mmm), D_{3h}(62m), D_{4h}(4/mmm), D_{6h}(6/mmm)$
dihedral with planes between axes	$D_{2d}(42m), D_{3d}(3m)$
improper rotation	$S_4(4), S_6(3)$
cubic groups	$T(23), T_h(m3), T_d(\bar{4}3m), O(432), O_h(m\bar{3}m)$

Table 3: The 32 crystallographic point groups. Labels are given in Schoenflies notation and Hermann-Mauguin notation in italic

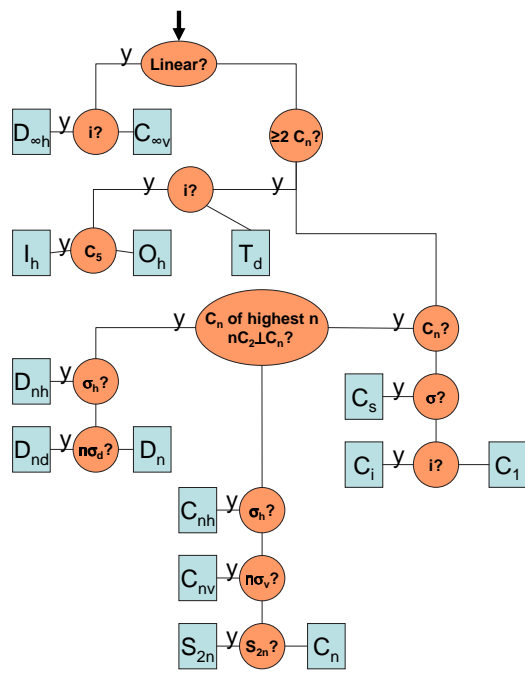


Figure 4: Flow chart to find the symmetry point group of a molecule

3 Theory of representation

3.1 Representation of a group

So far, we have seen that by studying the geometric properties of a molecule, one can find a set of symmetry operations that leave the molecule globally invariant. This set of operations, that can be regrouped in classes, has the structure of a group, called Point Group. Fine, but it hasn't help much to reduce a problem based on symmetry arguments. So, what is representation theory all about? Representation theory is about reducing group-theory problems to problems in linear algebra. The symmetry group of the molecule corresponds to what is known as an abstract group. However, one can construct a representation of this group in a vector space. We say that a group G is represented in a vector space E if we form a homomorphism Γ of G in a sub group of the group of linear transformations $GL(E)$:

$$\forall g \in G, g \mapsto \Gamma(g) \in GL(E) \tag{7}$$

$$\forall g, g' \in G, \Gamma(gg') = \Gamma(g)\Gamma(g') \tag{8}$$

$$\Gamma(\text{identity}) = \text{identity} \tag{9}$$

$$\forall g \in G, \Gamma(g^{-1}) = (\Gamma(g))^{-1} \tag{10}$$

If one forms a representation of a group in a finite vector space, say of dimension n , for which a basis has been chosen, then $\Gamma(g) \forall g$ in G can be represented by a $n \times n$ matrix. The set of matrices form a *representation* of the group. The dimension of the representation corresponds to the dimension of the vector space. Let's take the previous example, and construct a representation of the C_{2v} group: We consider a 3 dimensional space with a cartesian coordinate system, supported by a basis $(\vec{i}, \vec{j}, \vec{k})$. We can write down the matrices representing the transformation of a point P , of coordinates (x,y,z) , by operations of the C_{2v} group as follows:

$$\begin{aligned}
 E &\rightarrow \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} C_2(z) \rightarrow \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \\
 \sigma(xz) &\rightarrow \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \sigma(yz) \rightarrow \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}
 \end{aligned} \tag{11}$$

The set of matrices forms a *representation* of the group C_{2v} , of dimension 3. The law of composition between matrices is the multiplication. So the product of two operations in the symmetry group is represented by the the product of the corresponding transformation matrices in vector space. For example, according to the result of the multiplication table of the C_{2v} group, $C_2(z)\sigma(xz)=\sigma(yz)$ which hold with matrix representatives:

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \cdot \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{12}$$

Of course this is not the only representation of this group. Let change the vector space and consider the one formed by unit polar vectors centered on each atom of the H_2O molecule and directed along the 3 cartesian axis, as shown on figure 5. The vector space is now 9-dimensional. We can write the matrices representing the linear transformations of vector space, as follow:

$$E \rightarrow \left(\begin{array}{ccc|ccc} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ \hline 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ \hline 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{array} \right) \cdot \begin{pmatrix} xO \\ yO \\ zO \\ xH_1 \\ yH_1 \\ zH_1 \\ xH_2 \\ yH_2 \\ zH_2 \end{pmatrix} \quad (13)$$

$$C_2(z) \rightarrow \left(\begin{array}{ccc|ccc} -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ \hline 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ \hline 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{array} \right) \cdot \begin{pmatrix} xO \\ yO \\ zO \\ xH_1 \\ yH_1 \\ zH_1 \\ xH_2 \\ yH_2 \\ zH_2 \end{pmatrix} \quad (14)$$

$$\sigma(xz) \rightarrow \left(\begin{array}{ccc|ccc} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ \hline 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ \hline 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{array} \right) \cdot \begin{pmatrix} xO \\ yO \\ zO \\ xH_1 \\ yH_1 \\ zH_1 \\ xH_2 \\ yH_2 \\ zH_2 \end{pmatrix} \quad (15)$$

$$\sigma(yz) \rightarrow \left(\begin{array}{ccc|ccc} -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ \hline 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ \hline 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{array} \right) \cdot \begin{pmatrix} xO \\ yO \\ zO \\ xH_1 \\ yH_1 \\ zH_1 \\ xH_2 \\ yH_2 \\ zH_2 \end{pmatrix} \quad (16)$$

This is another representation of the group, of dimension 9. The two previous examples are constructed in vector spaces formed by polar vectors. But I would like to stress that a representation of a group can be constructed in any vector space, supported by any function. Let's consider the p atomic orbitals of the oxygen atom, in the group of the water molecule. The angular part of the wave functions can be written, in polar coordinates:

$$\begin{aligned}
p_x &= \frac{1}{2} \sqrt{\frac{3}{\pi}} \sin(\theta) \cos(\phi) \\
p_y &= \frac{1}{2} \sqrt{\frac{3}{\pi}} \sin(\theta) \sin(\phi) \\
p_z &= \frac{1}{2} \sqrt{\frac{3}{\pi}} \cos(\theta)
\end{aligned}$$

It is easy to determine the action of symmetry operators on this set of orbitals. For example, the two-fold axis leaves p_z invariant and transform p_x and p_y into respectively $-p_x$ and $-p_y$... Once again, we can form a representation of the group in the vector space supported by p_x, p_y and p_z . More generally, one can form a representation of a group in a vector space of any set of function $\{f(\mathbf{r})\}$, a symmetry operator g acting on a function $f(\mathbf{r})$ as follows: $g[f(\mathbf{r})] = f[g^{-1}\mathbf{r}]$. One could take many other examples. At this point, it is important to realize the generality of representation theory: in a sense it doesn't matter what is transformed under application of symmetry operations, as long as we understand **how** it is transformed.

3.2 Irreducible representation

For each symmetry group, there are a limited number of representations, called *irreducibles*, that are of fundamental significance in representation theory. To explain the concept of irreducible representation, I will start by reversing the problem. Let's suppose that we have formed two representations Γ_1 and Γ_2 of a finite group G , in two vector spaces E_1 and E_2 of dimension n_1 and n_2 , respectively. Each of this subspace is, of course, left invariant by G . We can construct a vector space E , that is the direct sum of the vector space E_1 and E_2 , noted $E_1 \oplus E_2$. Any vector of this space can be written as a unique linear combination of vectors of the two subspaces. We can then construct a representation Γ of the group G in the vector space E . Of course, because of this deliberate construction, we know that two subspaces of E are left invariant. When a representation leaves at least one of the subspace of E is invariant, we will say that the representation is reducible.

Definition:

A representation Γ of a group G in E is said to be reducible, if it leaves at least a sub-space of E invariant. Otherwise, the representation is irreducible. The representation is totally reducible if E can be written as direct sums of subspaces E_i , $E = \sum_{\oplus} E_i$.

Given a representation Γ of a group G , and a set of associated matrices $\{\Gamma(g), \forall g \in G\}$, the representation is reducible if one can find a similarity transformation (in other words a change of base) that reduces all the matrices $\Gamma(g)$ to similar block-diagonal form as seen below. The dimensions of the blocks

are the dimensions of the subspaces left invariant. We recall that for block-diagonal matrices, corresponding blocks of each matrices multiply separately.

$$\begin{pmatrix} \square & & & \mathbf{0} \\ & \square & & \\ & & \square & \\ \mathbf{0} & & & \square \end{pmatrix}$$

It is important to understand the concept of reducible and irreducible representations so I would like to illustrate it with very trivial examples. Once again, let's go back to the point group of water molecule, C_{2v} , and a representation of this group in the 3D vector space supported by a cartesian coordinate system. One can easily see that the components x, y and z are independently either transformed in themselves or their opposite by any operation of the group. So the 3 subspaces supported respectively by \vec{i} , \vec{j} and \vec{k} are invariants. Therefore the representation of the group C_{2v} in a 3D vector space, with basis $(\vec{i}, \vec{j}, \vec{k})$ is reducible in three 1-dimensional representations. Of course, this case is trivial, and one can verify that the matrices of the representation, in equation 11, are indeed block-diagonals each block being of dimension 1. Now let's take the same problem again but in a different base. As shown in figure 6, we rotate the coordinate system by 45° .

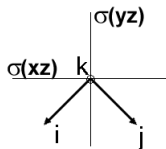


Figure 5: Point group C_{2v} with cartesian coordinate system rotated by 45° .

Of course in this base, the matrices are not block diagonal with the same form anymore:

$$\begin{aligned} E &\rightarrow \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} C_2(z) \rightarrow \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \\ \sigma(xz) &\rightarrow \begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \sigma(yz) \rightarrow \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \end{aligned} \tag{17}$$

However, we can find a similarity transformation (here the transition matrix T from this base to the previous one, shown below) that will bring all matrices

to the block-diagonal form of (11).

$$T = \begin{pmatrix} \frac{\sqrt{2}}{2} & \frac{\sqrt{2}}{2} & 0 \\ -\frac{\sqrt{2}}{2} & \frac{\sqrt{2}}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (18)$$

The main goal of representation theory is exactly that. Given a representation of a group in a vector space, is it possible to reduce the representation into irreducible representations, i.e. decompose the vector space in orthogonal subspaces of smaller dimensions? If yes, then what is the similarity transformation that allow to do that, i.e. what are the basis vectors that support each subspace. In the rest of the lecture, we will focus on these two points:

- 1) Decomposition of a reducible representation in irreducible representations
- 2) Construction of the basis functions

3.3 Character of a representation

The character of a representation Γ of a group G is a function χ that sends g in G to the trace of the matrix $\Gamma(g)$.

3.4 Character tables

The character table of a group G , is a table formed by the characters of all the irreducible representations of the group. The table is constructed as follows:

- The "conjugacy" classes of the group are displayed horizontally.
- The irreducible representations are listed vertically. The irreducible representations are sometimes labeled arbitrarily ($\Gamma_1, \Gamma_2, \dots$) or with symbols related to their symmetry properties (notation proposed by Mulliken).
- $\forall g \in G$, the character $\chi(g)$ of the representation is given in the corresponding table entry.

I have reported below the character tables for the point groups C_{2v} (symmetry group of the water molecule) and C_{3v} (symmetry group of the ammonia).

Here, we won't describe the mathematical procedure to construct the irreducible representations of a group. The irreducible representations for point groups are tabulated in a number of textbooks. Irreducible representations for space groups have been tabulated by Kovalev or can be calculated using program such as KAREP.

3.5 Decomposition in irreducible representations

3.5.1 Orthogonality theorem

There is an essential theorem in group theory, the orthogonality theorem, sometimes referred to as the Great Orthogonality Theorem (GOT) that will be given here without proofs. The proof can be found in Wagner or [?].

G is a group of order h , and Γ_i and Γ_j two irreducible representations of this group, of dimension l_i and l_j respectively. We will note $\Gamma_i(g)$ the matrix of representation i for the operation g . The corresponding matrix elements will be noted $\Gamma_i(g)_{\alpha\beta}$. The *character* of $\Gamma_i(g)$ (is noted $\chi_i(g)$). The orthogonality theorem states that:

$$\sum_{g \in G} \Gamma_i(g)_{\alpha\beta} \Gamma_j(g)_{\alpha'\beta'}^* = \frac{h}{\sqrt{l_i l_j}} \cdot \delta_{ij} \cdot \delta_{\alpha\alpha'} \cdot \delta_{\beta\beta'} \quad (19)$$

A number of important properties are derived directly from the GOT:

The sum of the squared characters of an irreducible representation equal the order of the group:

$$\sum_{g \in G} \chi_i(g)^2 = h \quad (20)$$

The sum of the product of characters of two inequivalent irreducible representations is null:

$$\sum_{g \in G} \chi_i(g) \chi_j(g) = 0 \quad (21)$$

3.5.2 Decomposition

The decomposition of a reducible representation into a sum of irreducible representations is a direct consequence of the orthogonality theorem. Let's suppose that a reducible representation Γ can be decomposed in irreducible representations :

$$\Gamma = \sum_k a_k \Gamma_k$$

Then,

$$\chi(g) = \sum_k a_k \chi_k(g) \forall g \in G$$

$$\sum_{g \in G} \chi(g) \chi_i(g) = \sum_k a_k \left(\sum_{g \in G} \chi_k(g) \chi_i(g) \right)$$

$$a_i = \frac{1}{h} \sum_{g \in G} \chi(g) \chi_i(g) \quad (22)$$

By applying formula 22 for all irreducible representations i of the group, one can find the coefficients of the decomposition. This step is straightforward, once we have constructed a representation of a group in a vector space, and calculate the character of this representation. Once again let's illustrate that with a few examples. First, the representation of the group C_{2v} in the vector space as described by 11.

C_{2v}	E	$C_2(z)$	$\sigma(xz)$	$\sigma(yz)$
A1	+1	+1	+1	+1
A2	+1	+1	-1	-1
B1	+1	-1	+1	-1
B2	+1	-1	-1	+1
Γ	3	-1	1	1

$$a_{A_1} = \frac{1}{4}(3 \times 1 - 1 \times 1 + 1 \times 1 + 1 \times 1) = 1$$

$$a_{A_2} = \frac{1}{4}(3 \times 1 - 1 \times 1 + 1 \times (-1) + 1 \times (-1)) = 0$$

$$a_{B_1} = \frac{1}{4}(3 \times 1 - 1 \times (-1) + 1 \times 1 + 1 \times (-1)) = 1$$

$$a_{B_2} = \frac{1}{4}(3 \times 1 - 1 \times (-1) + 1 \times (-1) + 1 \times 1) = 1$$

$$\Gamma = A_1 \oplus B_1 \oplus B_2$$

Now, if we consider the representation in the vector space supported by polar vectors of the water molecules and calculate the characters accordingly (matrices 13 to 16), one will find the following decomposition:

C2v	E	C2(z)	$\sigma(xz)$	$\sigma(yz)$
A1	+1	+1	+1	+1
A2	+1	+1	-1	-1
B1	+1	-1	+1	-1
B2	+1	-1	-1	+1
Γ	9	-1	3	1

$$a_{A_1} = \frac{1}{4}(9 \times 1 - 1 \times 1 + 3 \times 1 + 1 \times 1) = 3$$

$$a_{A_2} = \frac{1}{4}(9 \times 1 - 1 \times 1 + 3 \times (-1) + 1 \times (-1)) = 1$$

$$a_{B_1} = \frac{1}{4}(9 \times 1 - 1 \times (-1) + 3 \times 1 + 1 \times (-1)) = 3$$

$$a_{B_2} = \frac{1}{4}(9 \times 1 - 1 \times (-1) + 3 \times (-1) + 1 \times 1) = 2$$

$$\Gamma = 3A_1 \oplus A_2 \oplus 3B_1 \oplus 2B_2$$

3.6 Projection operators

Once the representation is decomposed in IRs, the second step consists in finding the basis vectors that support each of the invariant subspaces. In most cases it is not trivial to find the similarity transformation (or basis change) that send the matrices of the representation into block diagonal forms. To find these basic vectors (or symmetry adapted function), we use projection operators also called projectors:

$$\hat{P}_\lambda^\nu = \sum_{g \in G} D_{\lambda\mu}^\nu(g) \hat{g} \quad (23)$$

Here P is an operator that projects on the irreducible representation ν . $D_{\lambda\mu}^\nu(g)$ represent a matrix element of the IR ν and I have noted \hat{g} the operator corresponding to the operation g of the group. The idea is to apply this operator to an initial vector of the space E to find the components this space.

Here I like to treat an example where a representation of dimension 2 is involved. For this example, we suppose that we want to construct the Molecular Orbitals of the ammonia molecule in the LCAO (linear combination of atomic orbitals) approximation. Molecular orbitals are not directly obtained from atomic orbitals but rather from symmetry adapted linear combination of atomic orbitals. Because the N atom is not exchanged with the H atoms, we construct separately the symmetry adapted LCAO for the 3 hydrogen atoms.

So we are studying the representation of the point group C_{3v} in the vector space formed by three 1s atomic orbitals, noted s1, s2 and s3. The matrices are easily obtained:

$$\begin{aligned}
E &\rightarrow \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} C_3^1 \rightarrow \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} C_3^2 \rightarrow \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \\
\sigma_{v1} &\rightarrow \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \sigma_{(v2)} \rightarrow \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \sigma_{(v3)} \rightarrow \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}
\end{aligned} \tag{24}$$

You can verify that this representation is reducible and decomposed in $A_1 \oplus E$. Now let construct the symmetry adapted LCAO and for that use the projector operators. First projecting on A_1 :

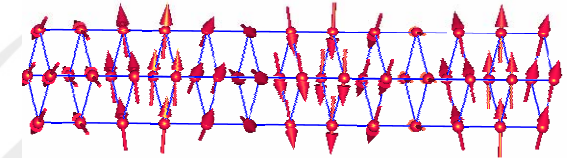
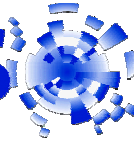
$$\begin{aligned}
\widehat{P}^{A_1} s1 &= \widehat{E} s1 + \widehat{C}_3^1 s1 + \widehat{C}_3^2 s1 + \widehat{\sigma}_{v1} s1 + \widehat{\sigma}_{v2} s1 + \widehat{\sigma}_{v3} s1 \\
\widehat{P}^{A_1} s1 &= s1 + s2 + s3 + s1 + s3 + s2 = 2(s1 + s2 + s3)
\end{aligned}$$

E is a 2-dimensional representation and therefore the character of the representation is no longer sufficient and one needs the matrices themselves. Below are reported the matrices for the doubly degenerate representation E :

$$E \rightarrow \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} C_3^1 \rightarrow \begin{pmatrix} -\frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix} C_3^2 \rightarrow \begin{pmatrix} -\frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix} \sigma_{v1} \rightarrow \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \sigma_{(v2)} \rightarrow \begin{pmatrix} -\frac{1}{2} & 0 \\ 0 & \frac{1}{2} \end{pmatrix} \sigma_{(v3)}$$



CC L R C **ISIS**



Magnetic structures: Formalism of propagation vector

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Rutherford Appleton Laboratory
Chilton, Didcot
UK

J. Rodriguez-Carvajal (LLB-France)



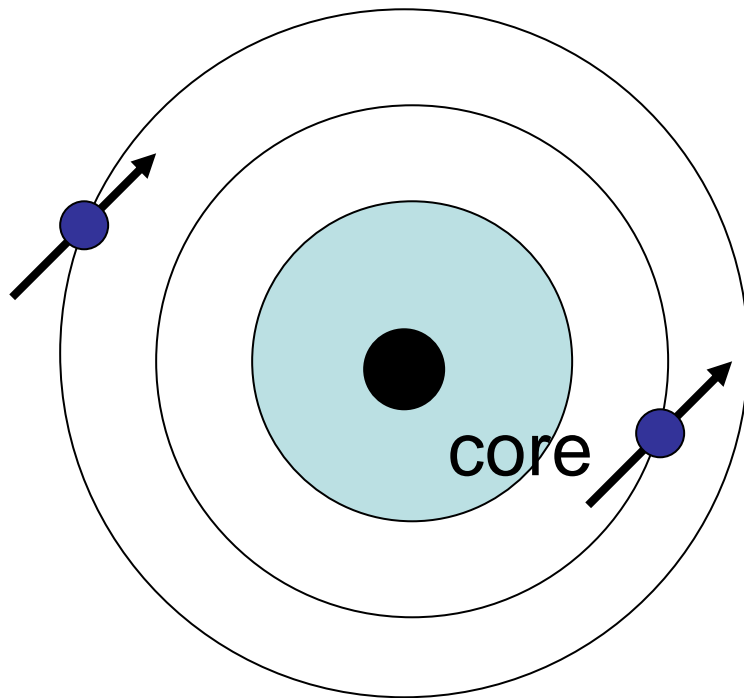
CENTRE NATIONAL
DE LA RECHERCHE
SCIENTIFIQUE



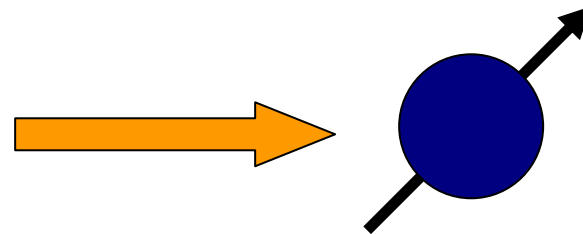
1. What's a magnetic structure?
2. How to describe magnetic structures with the formalism of propagation vector(s).
3. Plotting complex magnetic structure with FStudio.
4. Symmetry, symmetry, symmetry...
5. Strategy for solving magnetic structures, indexation, simulated annealing....

Atoms/ions with unpaired electrons

Intra-atomic electron correlation
Hund's rule: maximum S/J



Ni²⁺



$$\mathbf{m} = g_J \mathbf{J} \quad (\text{rare earths})$$

$$\mathbf{m} = g_S \mathbf{S} \quad (\text{transition metals})$$

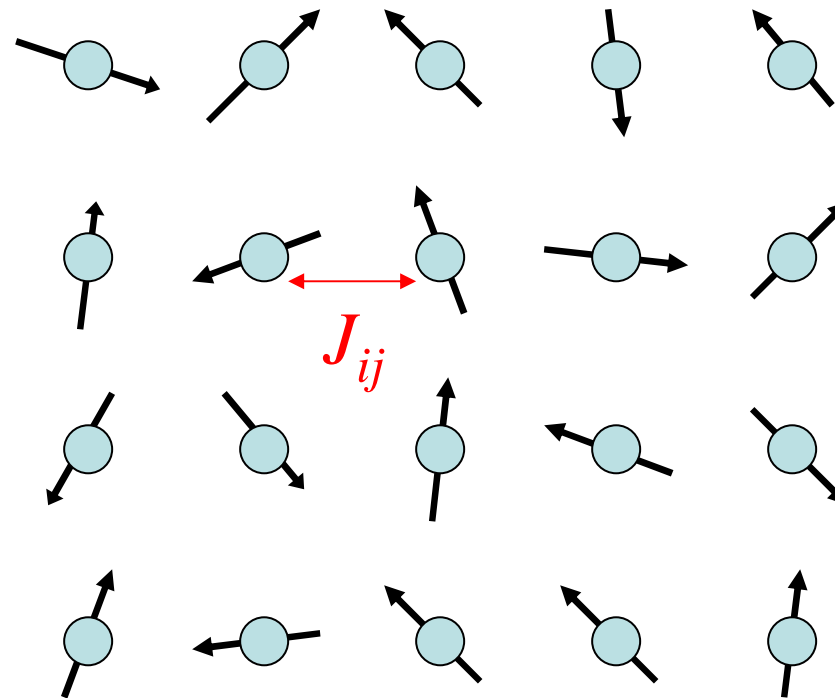
What is a magnetic structure?

Paramagnetic state:

Snapshot of magnetic moment configuration

$$E_{ij} = -J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$

$$\langle \mathbf{S}_i \rangle = 0$$

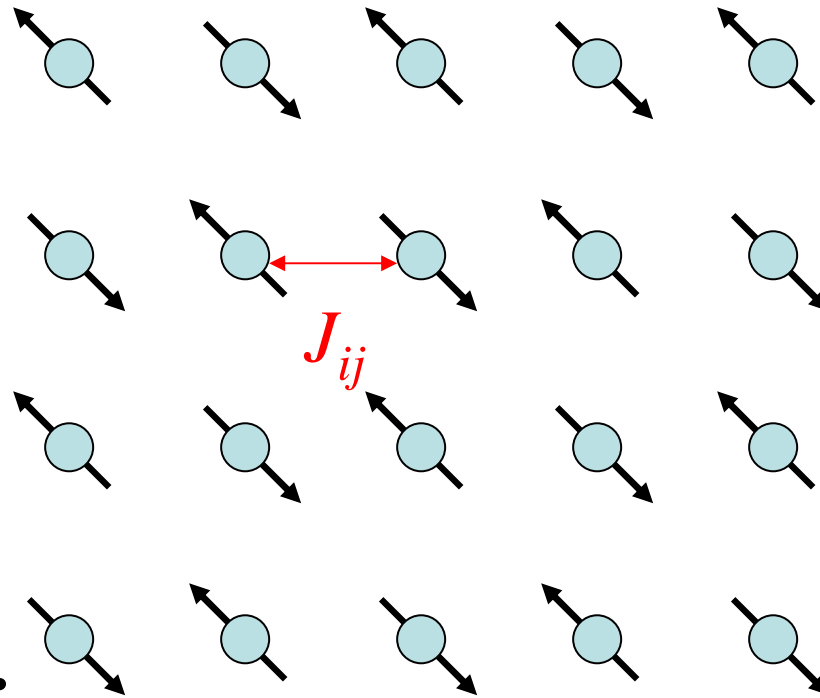


Ordered state: Anti-ferromagnetic

Small fluctuations (spin waves) of the static configuration

$$E_{ij} = -J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$

$$\langle \mathbf{S}_i \rangle \neq 0$$



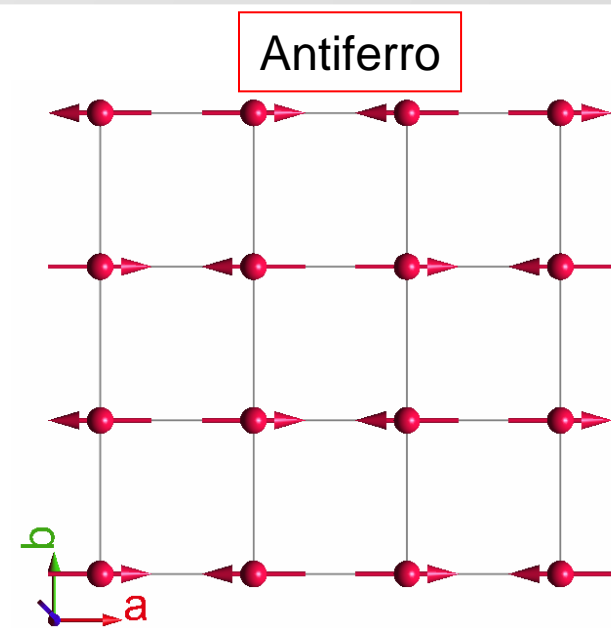
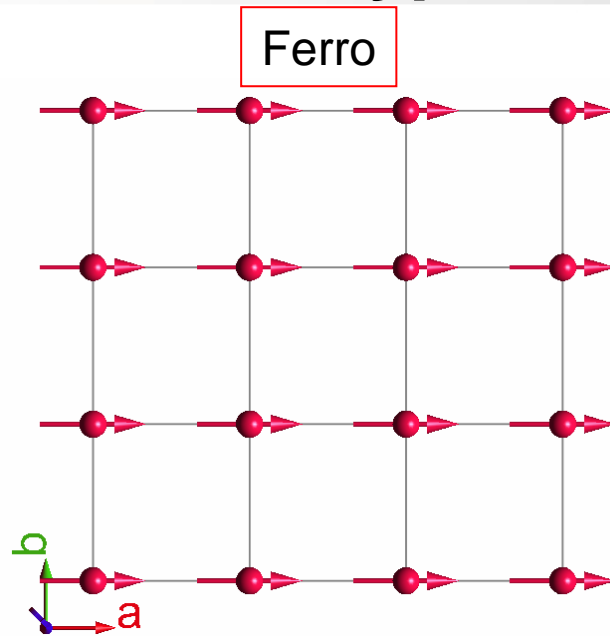
Magnetic structure:

Quasi-static configuration of magnetic moments



CCLRC

Types of magnetic structures



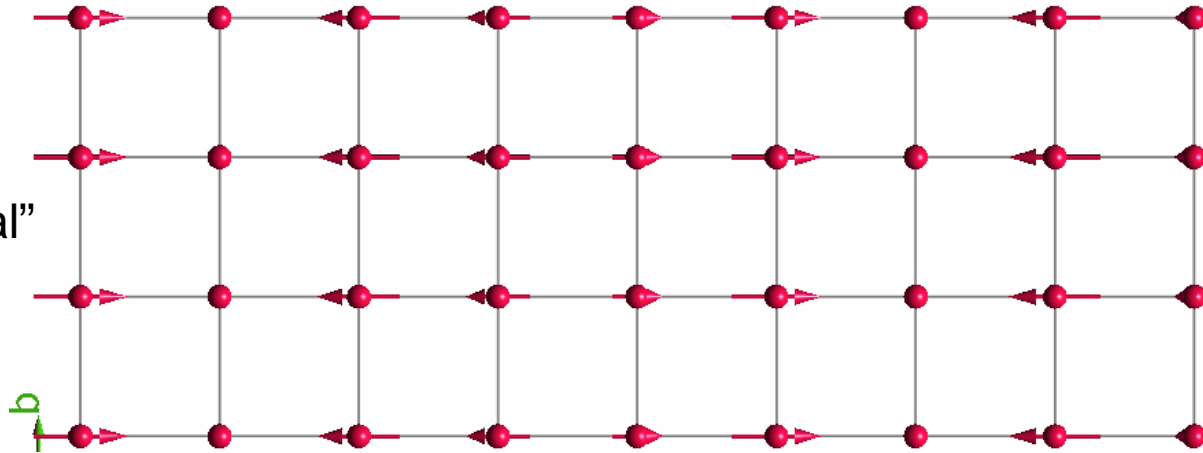
Very often magnetic structures are complex due to :

- competing exchange interactions (i.e. RKKY)
- geometrical frustration
- competition between exchange and single ion anisotropies
-

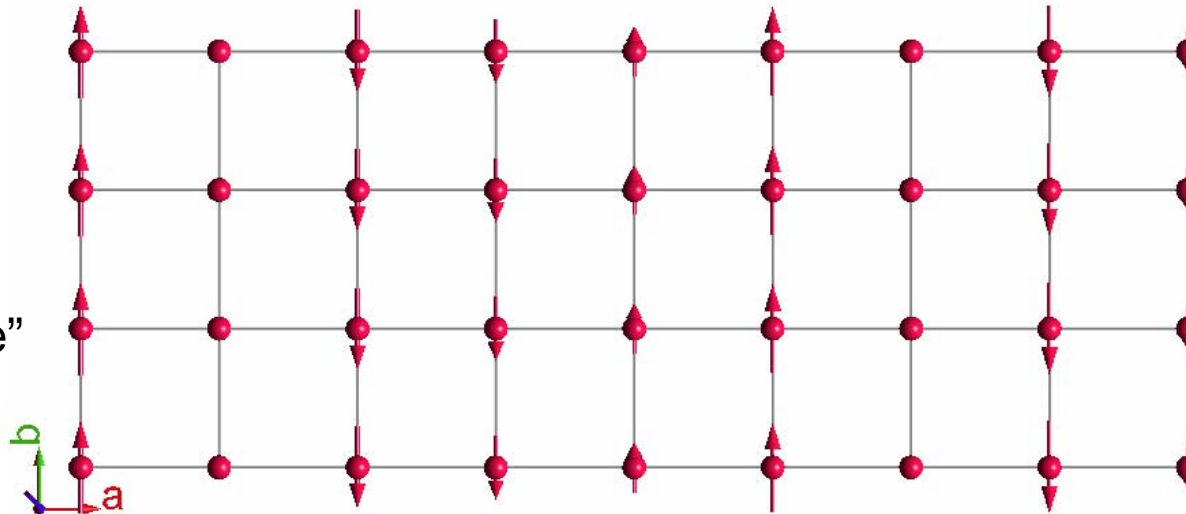
Types of magnetic structures

Amplitude-modulated or Spin-Density Waves

“Longitudinal”



“Transverse”



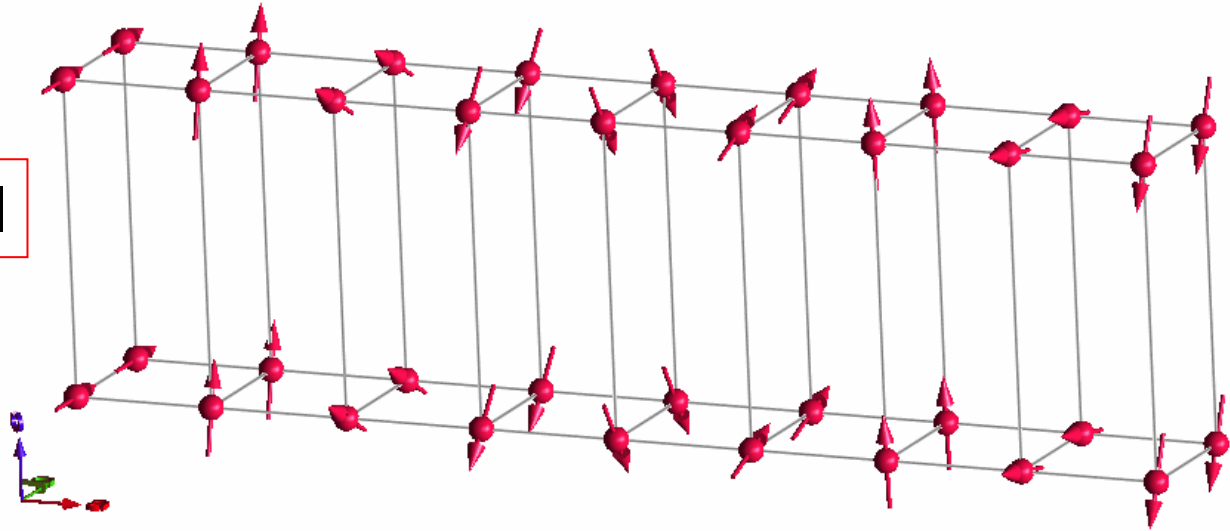
L.C. Chapon, Magnetism tutorial, ACNS 2006



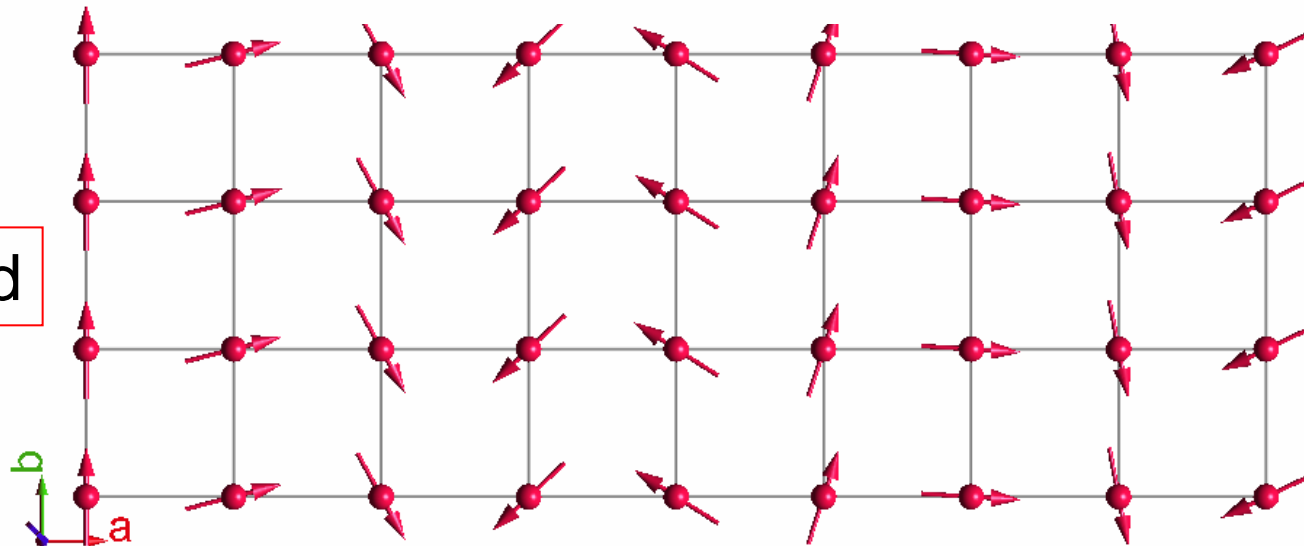
CCLRC

Types of magnetic structures

Spiral



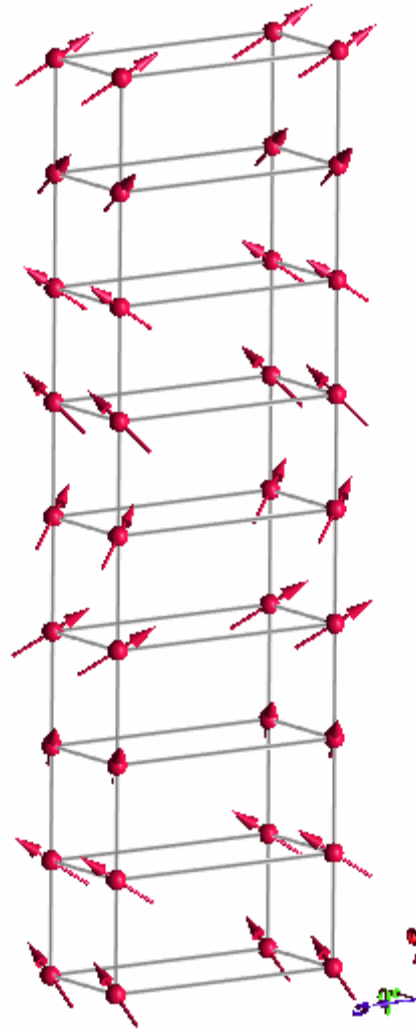
Cycloid



L.C. Chapon, Magnetism tutorial, ACNS 2006



Conical

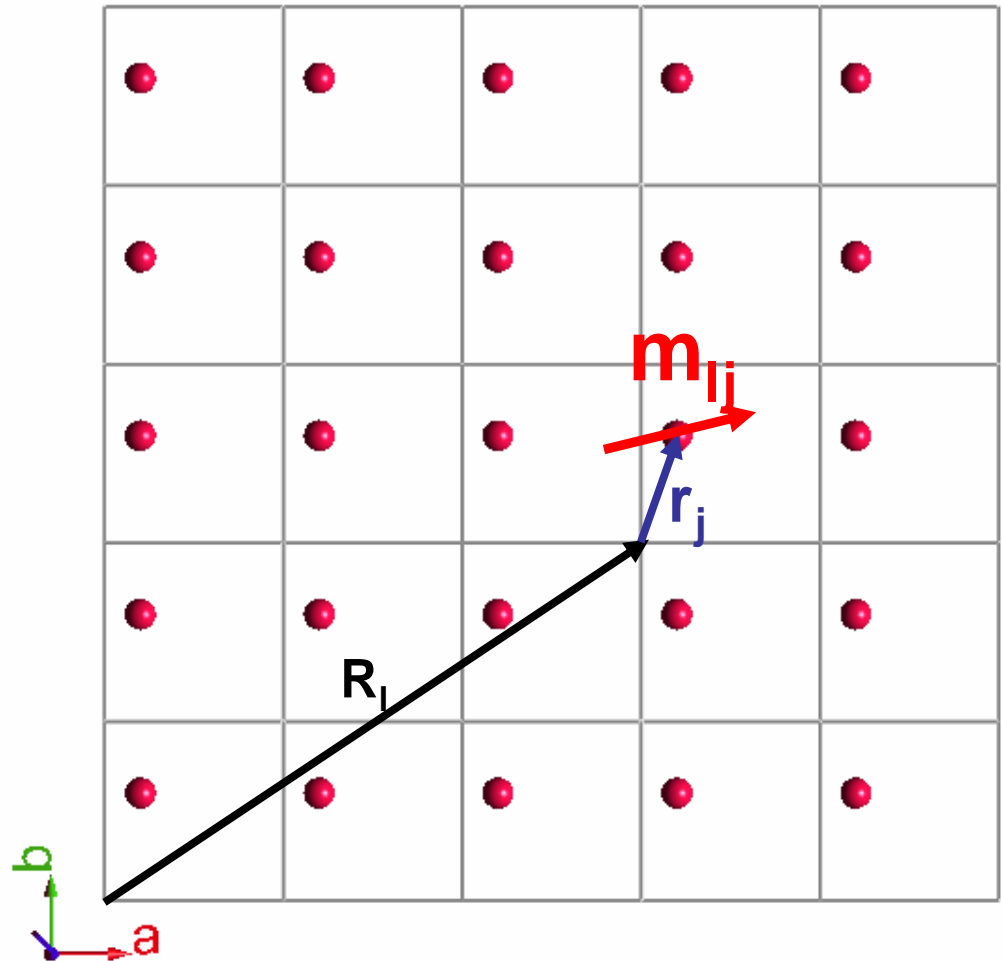


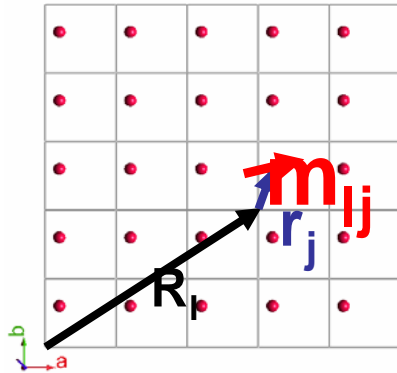
Shubnikov magnetic groups, are limited to:

- Commensurate magnetic structure.
- Real representation of dimension 1.

Position of atom j in unit-cell l is given by:

$R_{lj} = R_l + r_j$ where R_l is a pure lattice translation





$$\mathbf{m}_{lj} = \sum_{\{\mathbf{k}\}} \mathbf{S}_{\mathbf{k}j} \exp\{-2\pi i \mathbf{k} \mathbf{R}_l\}$$

$$\mathbf{R}_{lj} = \mathbf{R}_l + \mathbf{r}_j = l_1 \mathbf{a} + l_2 \mathbf{b} + l_3 \mathbf{c} + x_j \mathbf{a} + y_j \mathbf{b} + z_j \mathbf{c}$$

Necessary condition for real \mathbf{m}_{lj}

$$\mathbf{S}_{-\mathbf{k}j} = \mathbf{S}_{\mathbf{k}j}^*$$

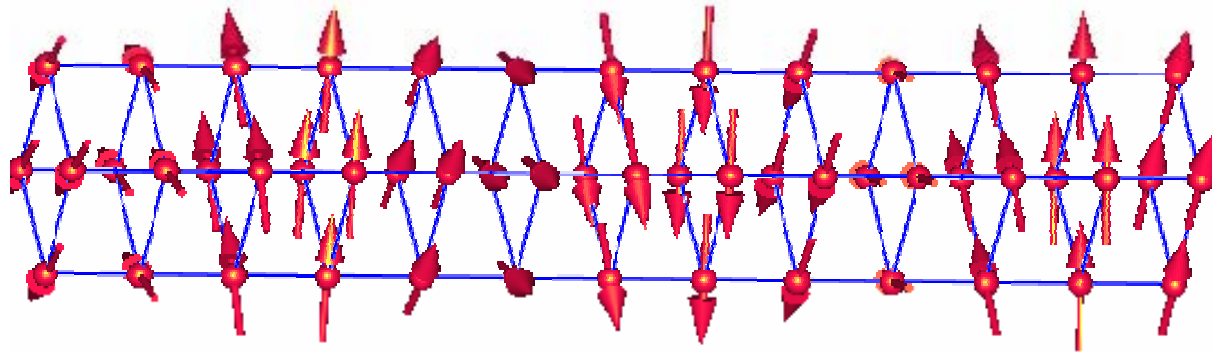


CCLRC

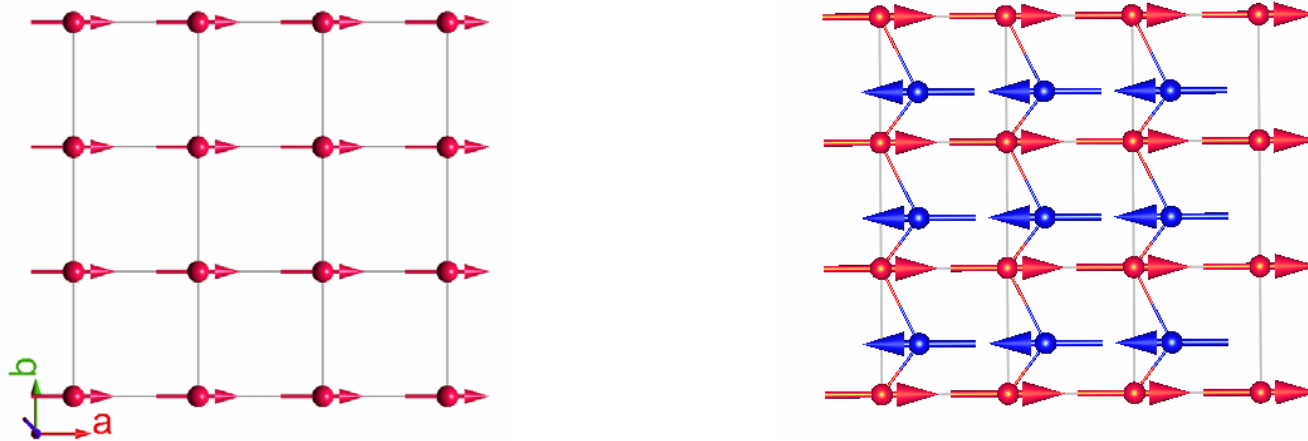
Formalism of prop. Vector : Basics

A magnetic structure is fully described by:

- Wave-vector(s) $\{k\}$.
- Fourier components \mathbf{S}_{kj} for each magnetic atom j and wave-vector k .
 \mathbf{S}_{kj} is a complex vector (6 components) !!!
- Phase for each magnetic atom j , Φ_{kj}



Single propagation vector $\mathbf{k} = (0,0,0)$

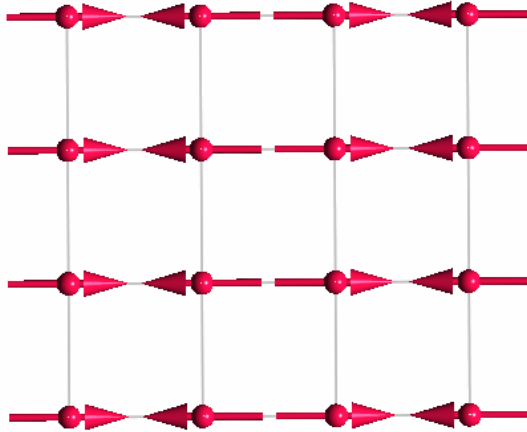


$$\mathbf{m}_{lj} = \sum_{\{\mathbf{k}\}} \mathbf{S}_{\mathbf{k}j} \exp\{-2\pi i \mathbf{k} \mathbf{R}_l\} = \mathbf{S}_{\mathbf{k}j}$$

- The magnetic structure may be described within the crystallographic unit cell
- Magnetic symmetry: conventional crystallography plus time reversal operator: crystallographic magnetic groups

Single propagation vector

$\mathbf{k} = 1/2 \mathbf{H}$



$$\mathbf{m}_{lj} = \sum_{\{\mathbf{k}\}} \mathbf{S}_{\mathbf{k}j} \exp\{-2\pi i \mathbf{k} \mathbf{R}_l\} = \mathbf{S}_{\mathbf{k}j} (-1)^{n(l)}$$

REAL Fourier coefficients \equiv magnetic moments

The magnetic symmetry may also be described using crystallographic magnetic space groups



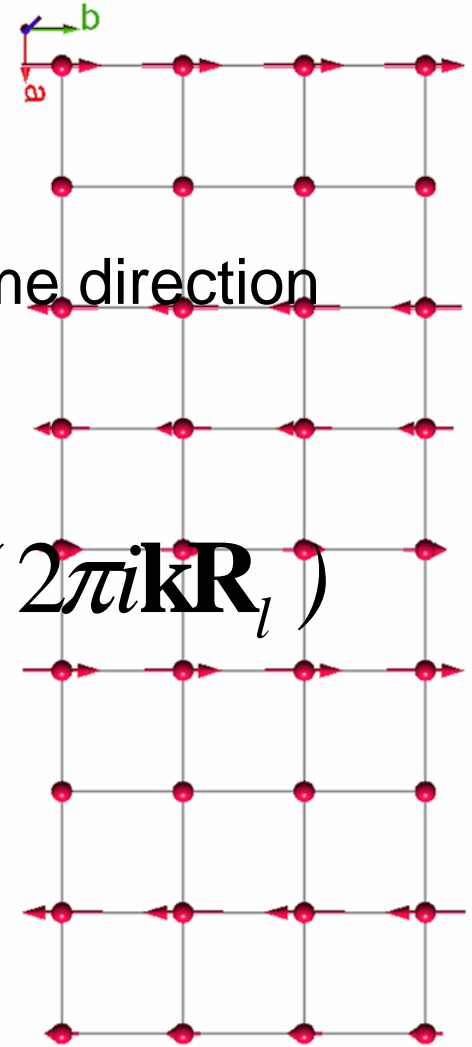
CCLRC Fourier coef. of sinusoidal structures

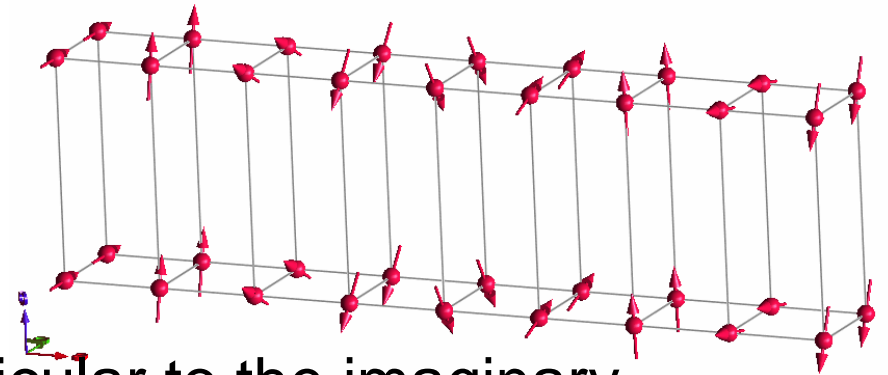
- k interior of the Brillouin zone (pair k , $-k$)
- Real S_k , or imaginary component in the same direction as the real one

$$\mathbf{m}_{lj} = \mathbf{S}_{\mathbf{k}j} \exp(-2\pi i \mathbf{k} \mathbf{R}_l) + \mathbf{S}_{-\mathbf{k}j} \exp(2\pi i \mathbf{k} \mathbf{R}_l)$$

$$\mathbf{S}_{\mathbf{k}j} = \frac{1}{2} m_j \mathbf{u}_j \exp(-2\pi i \phi_{\mathbf{k}j})$$

$$\mathbf{m}_{lj} = m_j \mathbf{u}_j \cos 2\pi(\mathbf{k} \mathbf{R}_l + \phi_{\mathbf{k}j})$$



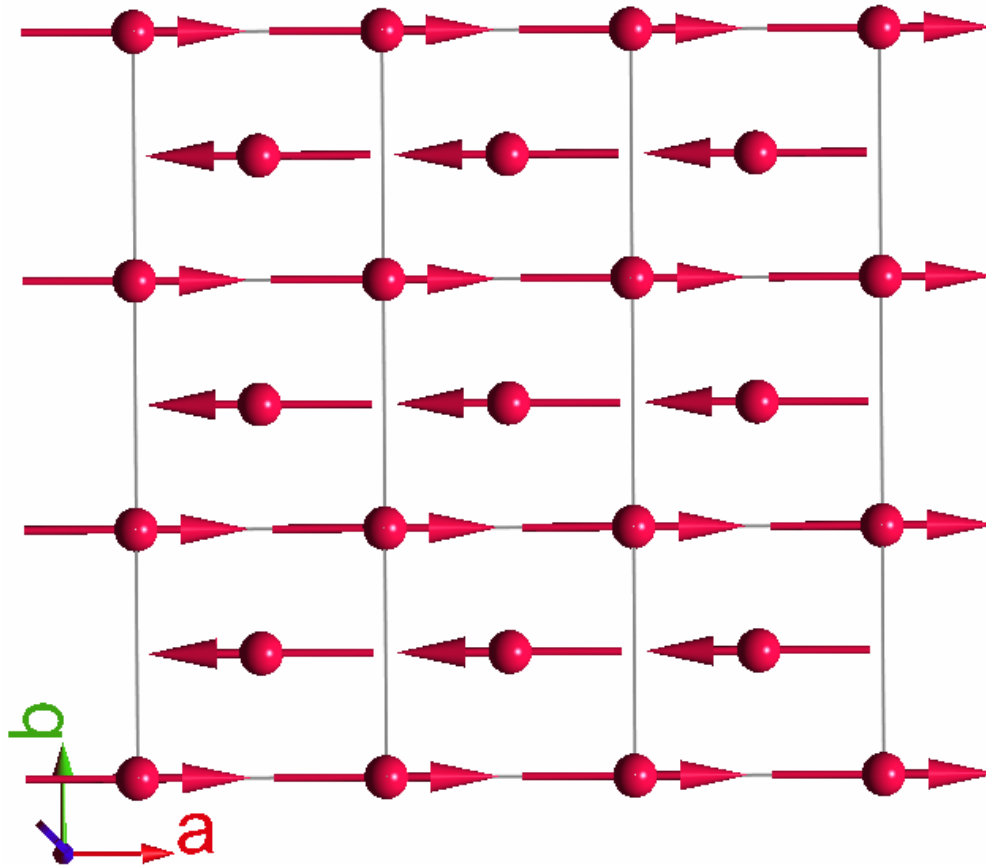


- \mathbf{k} interior of the Brillouin zone
- Real component of $\mathbf{S}_{\mathbf{k}}$ perpendicular to the imaginary component

$$\mathbf{S}_{\mathbf{k}j} = \frac{1}{2} \left[m_{uj} \mathbf{u}_j + i m_{vj} \mathbf{v}_j \right] \exp(-2\pi i \phi_{\mathbf{k}j})$$

$$\mathbf{m}_{lj} = m_{uj} \mathbf{u}_j \cos 2\pi(\mathbf{kR}_l + \phi_{\mathbf{k}j}) + m_{vj} \mathbf{v}_j \sin 2\pi(\mathbf{kR}_l + \phi_{\mathbf{k}j})$$

Centred cells!



$k=(1,0,0)$ or $(0,1,0)$!!!!!



www-llb.cea.fr/fullweb

```

{
LATTICE P
K 0.5 0.0 0.0
SYMM x,y,z
MSYM u,v,w,0.0
MATOM Ce1 CE 0.0 0.0 0.0
SKP 1 1 2.0 0.0 0.0 0.0 0.0 0.0 0.0
}

```

Type of lattice P, C, I, F.....

Propagation vector(s)

List of symmetry operators with associated magnetic operator

Magnetic atom

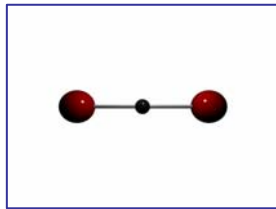
Fourier coefficients and phase

- Problem is underdetermined:
 - large number of parameters
(6 Fourier coefs.+phase per magnetic atom and per k)
 - usually few observations, especially in powder patterns.
 - Magnetic form factor

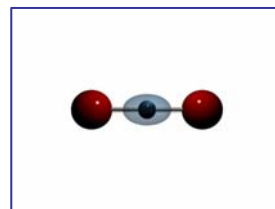
- Method for simplifying analysis of a problem in systems possessing some degree of symmetry.
- What is allowed vs. what is not allowed

Keyword : Invariance of the physical properties under application of symmetry operators.

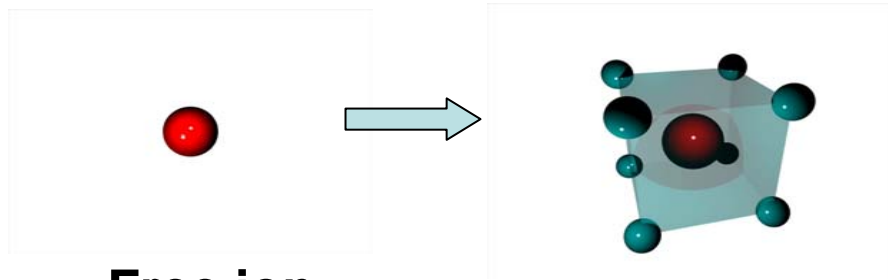
Spectroscopy



$$T = \int \phi^0 \mu \phi^1$$



$$T = \int \phi^0 \alpha \phi^1$$



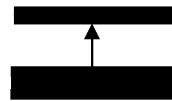
Free ion

Ground state multiplet

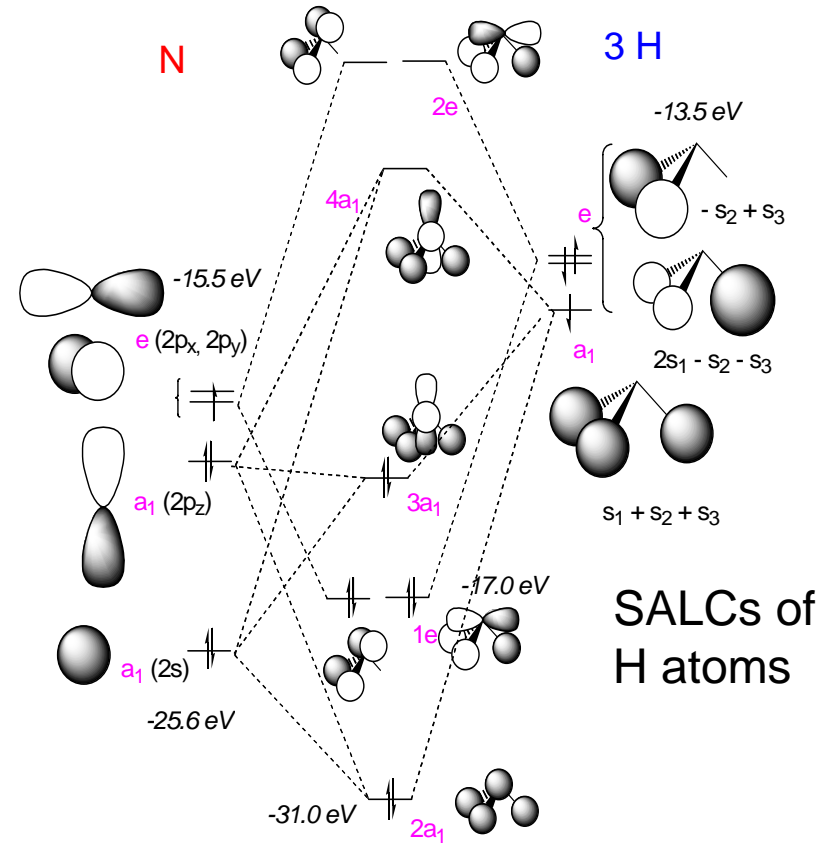


$$T = \int \phi^0 J_i \phi^1$$

$$\Delta J = 0; +1; -1$$



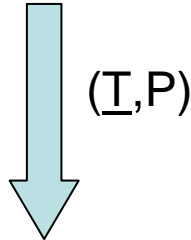
MO-LCAO



SALCs of H atoms

Phase transitions often take place between phases of different symmetry.

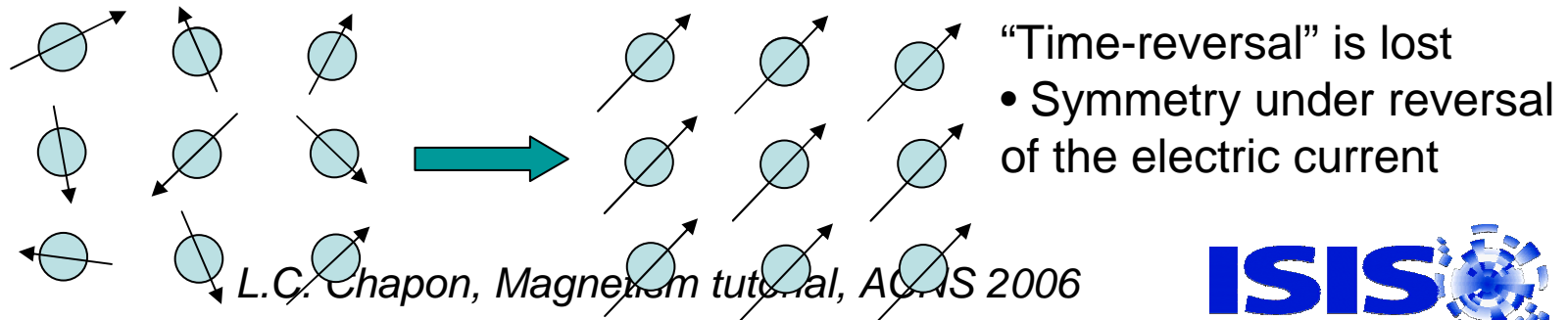
High symmetry phase, Group G_0



Low symmetry phase, Group G_1

- This is a “spontaneous” symmetry-breaking process.
- Transition are classified as either 1st order (latent heat) or 2^d order (or continuous)

A simple example: Paramagnetic -> Ferromagnetic transition



L.C. Chapon, Magnetism tutorial, AG-NS 2006

- Ordering is characterized by a function $\rho(x)$ that changes at the transition.
- Above T_c , $\rho_0(x)$ is invariant under all operations of G_0
- Below T_c , $\rho_1(x)$ is invariant under all operations of G_1

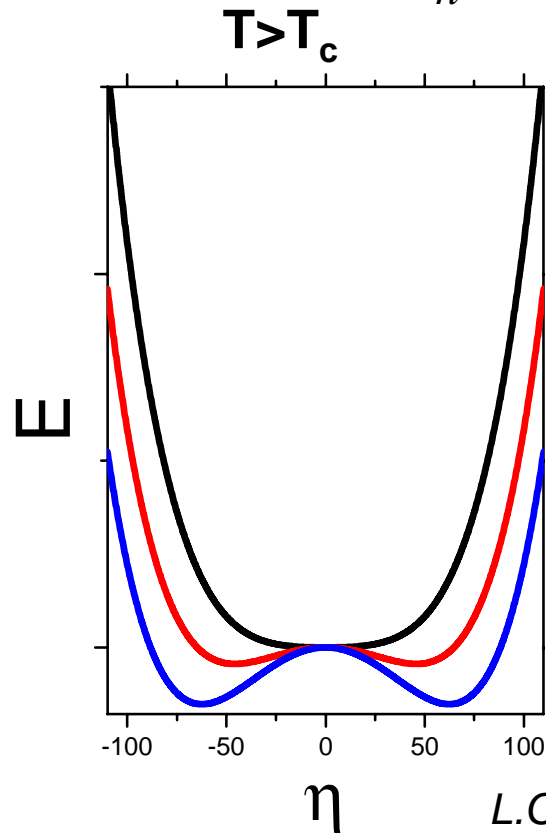
$$\delta\rho = \rho_1 - \rho_0 = \sum_{n'} \sum_i c_i^n \Phi_i^n(x) \longrightarrow \text{Basis functions of irreducible Representation of } G_0.$$

- At $T=T_c$, all the coefficients c_i^n vanish

Landau theory (2)

Φ is invariant under operations of G , each order of the expansion can be written is given by some polynomial invariants of c_i^n .

$$\Phi = \Phi_0 + \sum_{n'} A^n(P, T) \sum_i (c_i^n)^2 + \dots$$



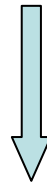
- Thermodynamic equilibrium requires that all A are >0 above T_c .
- In order to have broken symmetry, one A has to change sign at the transition.

$$\Phi = \Phi_0 + \frac{1}{2} a(T)(T - T_c) \eta^2 + C \eta^4 + \dots$$

In a second order phase transition, a single symmetry mode is involved.

Fourier coefficients as linear combinations of the basis functions of the irreducible representation of the propagation vector group $G_{\mathbf{k}}$

$$\mathbf{S}_{\mathbf{k}js} = \sum_{n\lambda} C_{n\lambda}^{\nu} \mathbf{S}_{n\lambda}^{\mathbf{k}\nu} (js)$$



$$\mathbf{M}(\mathbf{h}) = p \sum_{j=1}^n O_j f_j(\mathbf{h}) T_j \sum_{n\lambda} C_{n\lambda}^{\nu} \sum_s \mathbf{S}_{n\lambda}^{\mathbf{k}\nu} (js) \exp\{2\pi i[\mathbf{h}_s \mathbf{r}_j - \Phi_{\mathbf{k}j}]\}$$

$$\mathbf{S}_{\mathbf{k}js} = \sum_{n\lambda} C_{n\lambda}^{\nu} \mathbf{S}_{n\lambda}^{\mathbf{k}\nu} (js)$$

The coefficients $C_{n\lambda}^{\nu}$ are the free parameters of the magnetic structure (order parameters of the phase transition in the Landau theory)

Indices:

\mathbf{k} : reference to the propagation vector

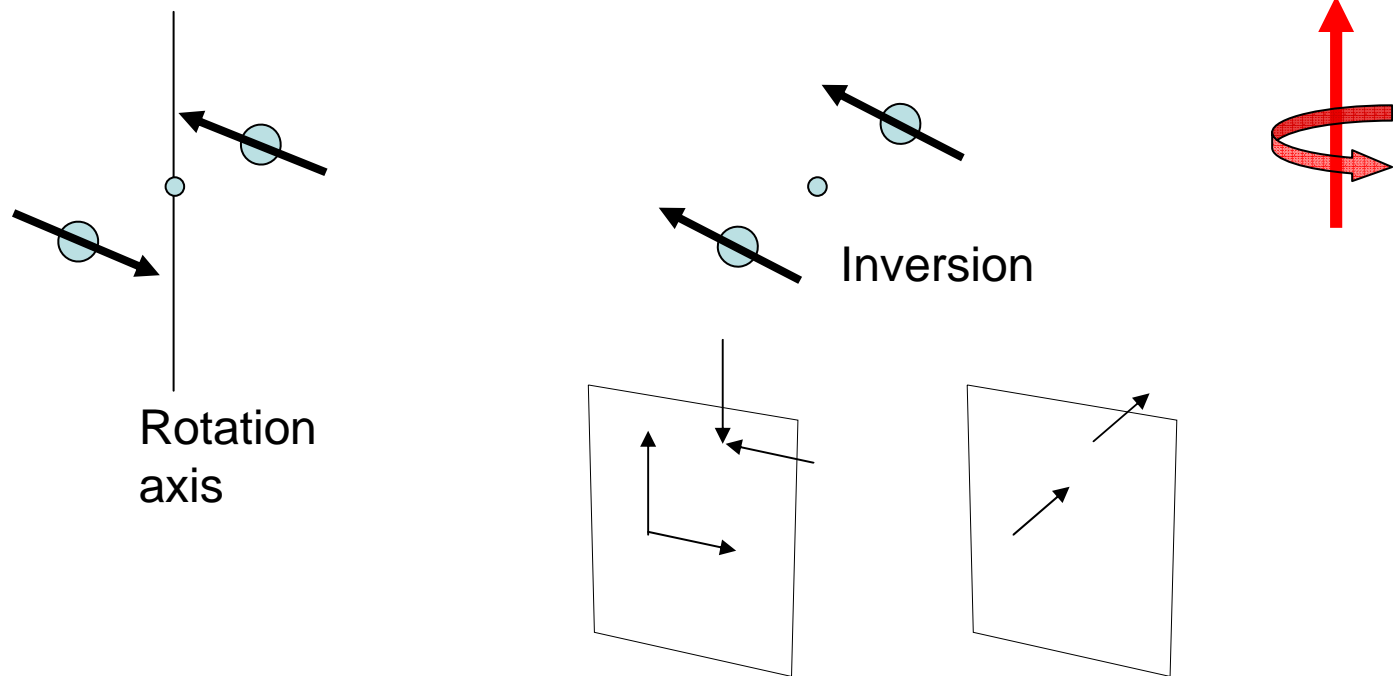
ν : reference to the irreducible representation Γ_{ν}

n : index running from 1 up to $n_{\nu} \Rightarrow \Gamma_{Mag} = \sum_{\oplus \nu} n_{\nu} \Gamma_{\nu}$

λ : index running from 1 up to $\dim(\Gamma_{\nu})$

Symmetry Analysis

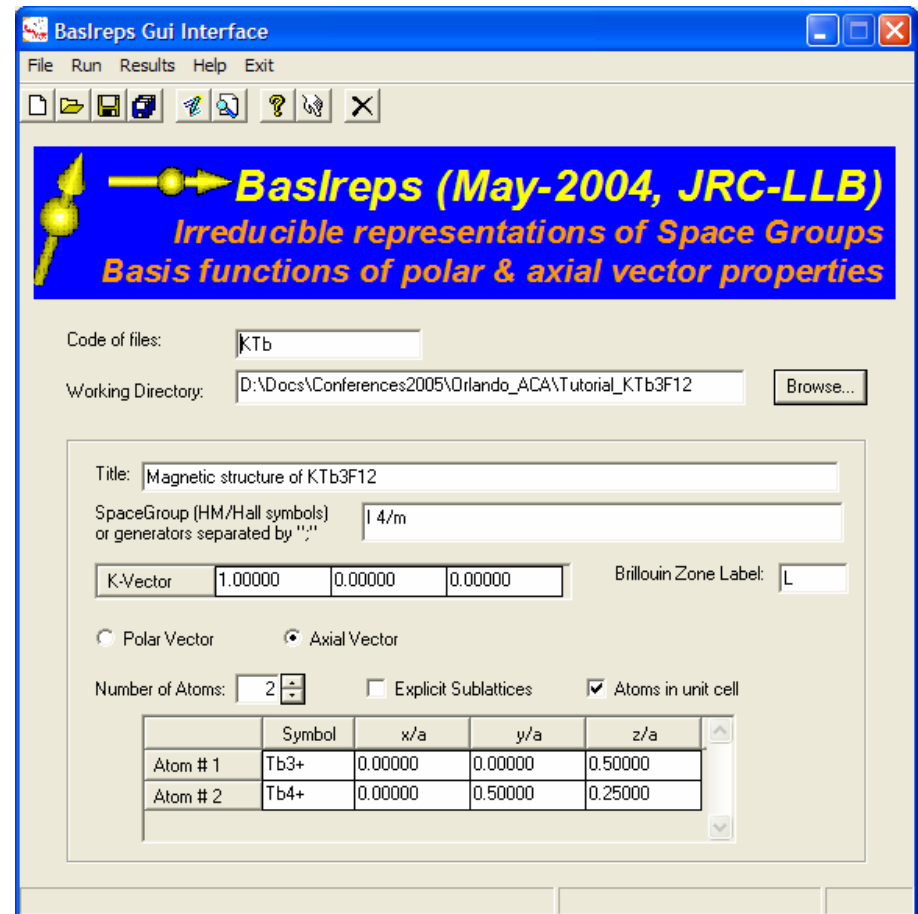
Magnetic moment is an axial (pseudo) vector.
Transformation under symmetry operation different to polar vector:



Kovalev's book:
 "Irreducible
 representations of space
 group"

Software:

- MODY
- SarAh
- Baslreps



Standard Fourier coefficients refinement:

A magnetic phase has $\mathbf{Jbt} = +/- 1$

$$\mathbf{M}(\mathbf{h}) = p \sum_{j=1}^n O_j f_j(\mathbf{h}) T_j \sum_s \mathbf{S}_{\mathbf{k}j_s} \exp\{2\pi i [(\mathbf{H} + \mathbf{k}) \{S|\mathbf{t}\}_s \mathbf{r}_j - \Phi_{\mathbf{k}j}]\}$$

The magnetic symmetry is introduced together with explicit symmetry operators of the crystal structure. The refined variables are directly the components of the $\mathbf{S}_{\mathbf{k}j_s}$ vectors



Standard Fourier components refinement

!-----
! Data for PHASE number: 2 ==> Current R_Bragg for Pattern# 1: 4.09
!-----

LaMnO3

!
!Nat Dis Mom Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth ATZ Nvk Npr More
1 0 0 0.0 0.0 1.0 1 0 -1 0 0 0.000 0 7 0

P m m m <--Space group symbol

!Nsym Cen Laue MagMat
4 1 3 1

!
SYMM x,y,z
MSYM u,v,w,0.0
SYMM -x,-y,z+1/2
MSYM -u,-v,w,0.0
SYMM -x+1/2,y+1/2,-z+1/2
MSYM u,-v,w,0.0
SYMM x+1/2,-y+1/2,-z
MSYM -u, v,w,0.0

!
!Atom Typ Mag Vek X Y Z Biso Occ Rx Ry Rz
! Ix Iy Iz beta11 beta22 beta33 MagPh
Mn1 MMN3 1 0 0.50000 0.00000 0.00000 0.04338 1.00000 0.000 3.847 0.000
0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 131.00 0.00
0.000 0.000 0.000 0.000 0.000 0.000 0.00000
0.00 0.00 0.00 0.00 0.00 0.00 0.00

L.C. Chapon, Magnetism tutorial, ACNS 2006



Coefficients of basis functions refinement:

A magnetic phase has $\mathbf{Jbt} = +/- 1$ and $\mathbf{Isy} = -2$

$$\mathbf{M}(\mathbf{h}) = p \sum_{j=1}^n O_j f_j(\mathbf{h}) T_j \sum_{n\lambda} C_{n\lambda}^{\nu} \sum_s \mathbf{S}_{n\lambda}^{\mathbf{k}\nu}(js) \exp\{2\pi i[\mathbf{h}_s \mathbf{r}_j - \Phi_{\mathbf{k}j}]\}$$

The basis functions of the Irreps (in numerical form) are introduced together with explicit symmetry operators of the crystal structure.

The refined variables are directly the coefficients C_1, C_2, C_3, \dots

$$\mathbf{S}_{\mathbf{k}js} = \sum_{n\lambda} C_{n\lambda}^{\nu} \mathbf{S}_{n\lambda}^{\mathbf{k}\nu}(js)$$

$$C_{n\lambda}^{\nu}$$

L.C. Chapoñ, Magnetism tutorial, ACNS 2006



CCLRC Basis functions coefficients refinement

```

LaMnO3
!
!Nat Dis Mom Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth      ATZ      Nvk Npr More
      1   0   0 0.0 0.0 1.0  1   0  -2   0   0      0.000    0   7   0
!
P m m m                      <--Space group symbol
! Nsym   Cen   Laue Ireps N_Bas
      4     1     1     -1     3
! Real(0)-Imaginary(1) indicator for Ci
      0   0   0
!
SYMM x,y,z
BASR   1   0   0   0   1   0   0   0   1
BASI   0   0   0   0   0   0   0   0   0
SYMM -x+1,-y,z+1/2
BASR  -1   0   0   0  -1   0   0   0   1
BASI   0   0   0   0   0   0   0   0   0
SYMM -x+1/2,y+1/2,-z+1/2
BASR   1   0   0   0  -1   0   0   0   1
BASI   0   0   0   0   0   0   0   0   0
SYMM x-1/2,-y+1/2,-z
BASR  -1   0   0   0   1   0   0   0   1
BASI   0   0   0   0   0   0   0   0   0
!
!Atom Typ   Mag Vek      X      Y      Z      Biso   Occ      C1      C2      C3
!      C4     C5      C6      C7      C8      C9      MagPh
Mn1  MMN3   1   0  0.50000 0.00000 0.00000 0.04338 1.00000  0.000  3.847  0.000
      0.00  0.00  0.00  0.00  0.00  0.00  0.00  0.00  0.00 131.00  0.00
      0.000 0.000 0.000 0.000 0.000 0.000 0.00000
      0.00  0.00  0.00  0.00  0.00  0.00  0.00

```

L.C. Chapon, Magnetism tutorial, ACNS 2006



StepPropagation vector(s) *SuperCell*Symmetry Analysis *Baslreps*Magnetic structure solution (Sim.
Ann.)
*FullProf***Input***Peak positions of
⇐ magnetic reflections
Cell parameters**Propagation vector
⇐ Space Group
Atom positions**Integrated intensities
⇐ Atomic components
of basis functions*

Program: *SuperCell* (J.Rodríguez-Carvajal, LLB-December-1998)

- This program can be used to index superstructure reflections from a powder diffraction pattern.
- The first approach consist in **searching the best "magnetic unit cell"** compatible with a set of observed SUPERSTRUCTURE lines in the powder diffraction pattern.
- If the **first approach fails** to give a suitable solution, the superstructure may be incommensurate and **a direct search for the propagation vector and one of its harmonics have to be used.**

Simulated Annealing (SA):

The SA method is a general purpose optimisation technique

for large combinatorial problems introduced by:

Kirpatrick, Gelatt and Vecchi, *Science* **220**, 671-680 (1983).

The function, $E(\omega)$ to be optimised with respect to the configuration described by the vector state ω is called the “cost” function.

Simulated Annealing (SA):

The SA method applied to structural problems:

- J. Pannetier, J. Bassas-Alsina, J. Rodríguez-Carvajal and V. Caignaert, *Nature* **346**, 343-345 (1990)
- J.M. Newsam, M.W. Deem and C.M. Freeman, Accuracy in Powder Diffraction II. NIST Special Publ. No. **846**, 80-91 (1992)
- J. Rodríguez-Carvajal, *Physica B* **192**, 55-69 (1993) (program MAGSAN)

Simulated Annealing (SA):

Minimize a cost function, energy $E(\omega)$, with respect to the configuration vector ω .

Origin: Monte Carlo methods for simulating properties of liquids (Metropolis algorithm)

**Algorithm trying to mimic the process of annealing a sample to obtain a good crystalline state (ground state):
A temperature schedule (starting high temperature + cooling rate) is needed.**

Procedure to generate new configurations (Markov chain) and a Boltzmann probability to explore the phase space (importance sampling)

begin

Initialise (set to zero useful quantities, do preliminary calculations)

$t = 1$

do

do

Perturb the system:

$\omega_{\text{old}} \rightarrow \omega_{\text{new}}, \Delta = E(\omega_{\text{new}}) - E(\omega_{\text{old}})$

if $\Delta \leq 0$ then **accept**, else

if $\exp(-\Delta/T_t) > \text{random}[0,1]$ then **accept**

if **accept** then **Update** (replace ω_{old} by ω_{new})

until equilibrium is approached closely enough (Ncyc)

$T_{t+1} = f(T_t)$ (decrease temperature, usually $T_{t+1} = q T_t, q \approx 0.9$)

$t = t + 1$

until stop criterion is true (maximum t , convergence, low % accepted...)

end

Simulated Annealing for magnetic structures:

- Look directly for the components of S_k and phases, explaining the experimental data
- Minimize a reliability factor with respect to the “configuration vector”

$$\boldsymbol{\omega} = |C_1, C_2, C_3, C_4, C_5, \dots, C_m\rangle$$

$$R_m(\boldsymbol{\omega}) = c \sum_{r=1}^N \left| G_{obs}^2(\mathbf{h}_r) - G_{calc}^2(\mathbf{h}_r, \boldsymbol{\omega}) \right|$$



CCLRC

Simulated Annealing run of *FullProf*

```
FullProf.2k_Multi_Pattern
=> *****
=> ** PROGRAM FullProf.2k (Version 2.40 - May2003-LLB JRC) **
=> *****
=>           M U L T I  -- P A T T E R N
=>           Rietveld, Profile Matching & Integrated Intensity
=>           Refinement of X-ray and/or Neutron Data
=>           (Multi_Pattern: Windows-version)

=> START Date:10/07/2003  Time => 07:24:51.793
=> Reading control file *.PCR ...
=> End of preliminary calculations !

=> **** SIMULATED ANNEALING SEARCH FOR STARTING CONFIGURATION ****

=> Initial configuration cost:      40.49
=> Initial configuration state vector:
=>   Rmom_Mn1 RPhi_Mn1 RPhi_Mn1 RPhi_Mn2 RPhi_Mn2
=>         1         2         3         4         5
=>   2.3146 156.3578 152.2612 319.1841  73.4829
=> NT:  1 Temp: 10.00 (%Acc): 51.40 <Step>:288.8000 <R-factor>: 53.6836
=> NT:  2 Temp:  9.00 (%Acc): 47.00 <Step>:288.6956 <R-factor>: 50.6513
=> NT:  3 Temp:  8.10 (%Acc): 45.60 <Step>:288.3760 <R-factor>: 45.8823
=> NT:  4 Temp:  7.29 (%Acc): 39.20 <Step>:288.3134 <R-factor>: 43.0660
```





CCLRC

Simulated Annealing run of *FullProf*

```
FullProf.2k_Multi_Pattern
=> NT: 69 Temp: 0.01 (%Acc): 42.40 <Step>: 0.2036 <R-factor>: 13.3120
=> NT: 70 Temp: 0.01 (%Acc): 40.60 <Step>: 0.1972 <R-factor>: 13.3079
=> NT: 71 Temp: 0.01 (%Acc): 41.60 <Step>: 0.1710 <R-factor>: 13.3025
=> NT: 72 Temp: 0.01 (%Acc): 46.60 <Step>: 0.1551 <R-factor>: 13.2982
=> NT: 73 Temp: 0.01 (%Acc): 35.80 <Step>: 0.1404 <R-factor>: 13.2960

=>BEST CONFIGURATIONS FOUND BY Simulated Annealing FOR PHASE:      1
=> -> Configuration parameters ( 150 reflections):

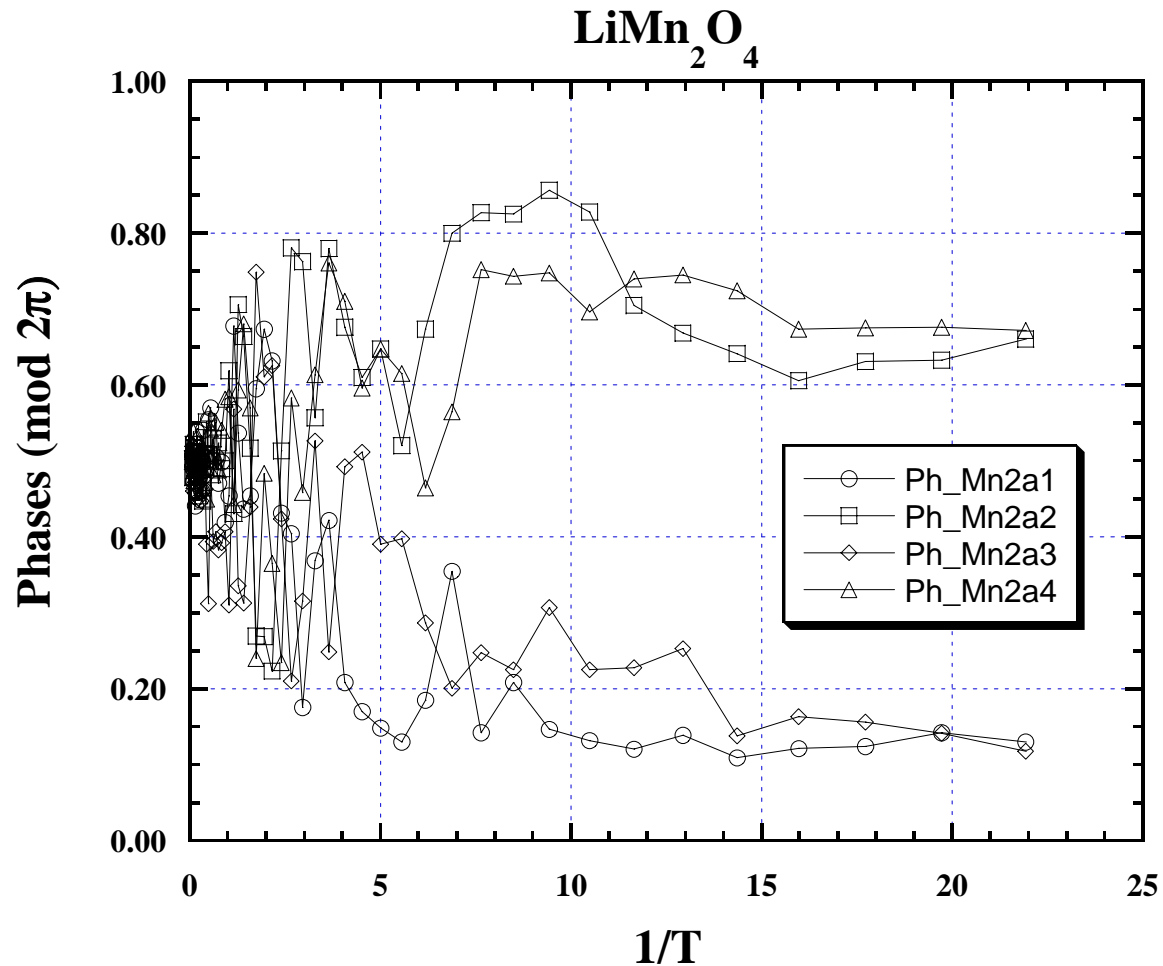
=> Sol#: 1 RF2= 13.282 ::
=>   Rmom_Mn1 RPhi_Mn1 RPhi_Mn1 RPhi_Mn2 RPhi_Mn2
=>         1         2         3         4         5
=>       2.9250  53.2323 324.9417 217.1961 144.8587

=>           CPU Time:      48.610 seconds
=>           0.810 minutes

=> END   Date:10/07/2003   Time => 07:25:40.413

=> Data Files :
=>   - simann
=> PCR File   : simann-t
```

Behavior of parameters in Simulated Annealing runs



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Average step ... Corana algorithm

