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Orientalional disorder in plastic molecular crystals

I. — Group theory and ODIC description

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Résumé. — Cet article présente une méthode de théorie des groupes pour construire une base canonique (complète et non redondante) de fonctions adaptée à la description du désordre orientationnel dans les cristaux moléculaires plastiques (ODIC). Cette méthode prend complètement en compte les propriétés des groupes de symétrie du site et de la molécule. En particulier, on montre que lorsque les deux groupes contiennent des rotations impropres, la base canonique comporte certaines fonctions qui jusqu'alors n'ont pas été prises en considération.

Abstract. — A group theory method for deriving a complete and non redundant canonical set of basis functions adapted to the description of Orientational Disorder In (plastic molecular) Crystal (ODIC) is developed. The method takes full advantage of the properties of the site and molecular symmetry groups. In particular, it is shown that, when both groups contain improper rotations, the canonical basis includes functions which have not been previously considered.

1. Introduction. — Plastic crystals can be defined as molecular crystals in which the orientational order of the molecules *melts* at a lower temperature than the translational order : below the transition temperature T_c each molecule has a given, fixed orientation, while above T_c , this orientation changes from molecule to molecule.

This high temperature phase may nevertheless vary between two extremes. Let us define an orthonormal axis system $\{X, Y, Z\}$ attached to the crystal and another one $\{x, y, z\}$ attached to the molecule. The molecular orientation can be described by the rotation Ω which brings the crystal system $\{X, Y, Z\}$ in coincidence with the molecular system $\{x, y, z\}$, i.e. by the set $[\Omega] \equiv \{\alpha, \beta, \gamma\}$ of the three Eulerian angles associated with this rotation in the crystal axes.

In the following, we shall, for brevity, call *pdf* (probability density function) the function $P_0([\Omega])$ which is the probability density for a molecule to have the orientation Ω .

— In one extreme case (e.g. phase I of CD_4 [1]) the molecules are almost completely at random, i.e. the *pdf* $P_0([\Omega])$ is equal to $1/8 \pi^2$ whatever is Ω .

— The other extreme case, represented e.g. by the ammonium halides [2] is characterized by the fact that, in the high temperature phase, only a discrete

set of values is available for $[\Omega]$. Such crystals are usually called disordered crystals and the n possible orientations are labelled according to the $n\sigma_z$ states of a $(n-1)/2$ spin. The thermodynamics and dynamics of the system in both phases are then written as functions of those spin variables, the disordered state being characterized by $\langle \sigma_z \rangle = 0$.

The very important intermediate cases have recently deserved a large interest, and some measurements of $P_0([\Omega])$ or, at least, of some of its components in e.g. phase I of CNNa [3] and CBr_4 [4] have been performed.

As $P_0([\Omega])$ plays a role analogous to the spin variable, but is, even in the plastic phase, a temperature dependent quantity, it is necessary to express it in a way which makes as transparent as possible its temperature dependence. The purpose of this paper is to provide, for a molecule of symmetry $\mathcal{M}$, residing in a site of symmetry $\mathcal{S}$, a systematic way of developing the *pdf* $P_0([\Omega])$ on a complete and non redundant basis of functions of $[\Omega]$. The various coefficients of the development will then appear as *a priori* independent long range order parameters of the plastic phase, the purpose of a thermodynamic treatment being of eventually predicting their temperature dependence, and the relationship between their values at a given temperature.

The *a priori* independence of the different order parameters lies on the non redundancy character of the set of basic functions. This is related to the symme-

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try properties of the *pdf* $P_0([\Omega])$ arising from both the molecular symmetry and the site symmetry. We shall see in this paper how the consideration of these both types of symmetry allows to define a set of symmetry adapted functions $\Delta_i^{\lambda\lambda'}([\Omega])$ suitable for the development of $P_0([\Omega])$:

$$P_0([\Omega]) = \sum_{i\lambda\lambda'} A_i^{\lambda\lambda'} \Delta_i^{\lambda\lambda'}([\Omega]) . \quad (1.1)$$

Symmetry adapted functions have already been introduced in several papers dealing with quantum mechanical studies of molecular crystals (see e.g. Refs. [5-9]). Indeed, our problem is somewhat equivalent to that of finding the general form of a monomolecular Hamiltonian in the framework of a molecular field approximation. Nevertheless, we think it is useful to recall here most of the theoretical background involved in such a development for two main reasons. First we shall stress the compatibility relation existing between the site symmetry group and the molecular symmetry and the crucial role played by improper rotations. Second, when both symmetry groups contain improper rotations, functions which are not usually considered appear in the development (1.1). Group theoretical arguments explain why the measurement of the corresponding coefficients is not straightforward and we shall deal with this problem in a following paper.

Part 2 is devoted to a close study of the symmetry properties of the probability $P_0([\Omega])$ and we shall derive in this part the full symmetry group $\mathcal{S}$ of this function. The knowledge of this group allows a straightforward construction of the symmetry adapted functions, however, we shall adopt in part 3 a different way allowing to classify these basic functions according to the irreducible representations of both the site group and the molecular group. In part 4 we shall apply this general formalism to some particular cases of molecular and site symmetries. At last, concluding remarks are included in part 5.

2. Symmetry properties of the probability $P_0([\Omega])$. —
2.1 PROPERTIES OF $P_0([\Omega])$. — As mentioned above, the orientation of one molecule in the crystal is represented by the rotation Ω which brings the crystal system axis $\{X, Y, Z\}$ in coincidence with the axis $\{x, y, z\}$ attached to the molecule. A physical rotation r will therefore simply bring a molecule from the orientation Ω to the orientation $r\Omega$.

By definition, the probability density function for molecular orientation, $P_0([\Omega])$, is a positive and real function, the integral of which over the whole space of possible orientations must be equal to unity. However we shall here focus our attention only on the symmetry properties of $P_0([\Omega])$ which arise both from the site symmetry and from the molecular symmetry.

The site symmetry is represented by a point group $\mathcal{S}$; subgroup of all the operations ρ of the crystallographic space group which leaves the site unchanged.

The molecular symmetry is described by a point group $\mathcal{M}(\Omega)$ the operations of which, $\rho'(\Omega)$, are defined in the molecular system axes and therefore depend on the orientation Ω of the molecule under consideration. To avoid this difficulty, we shall often refer to the symmetry group $\mathcal{M}$ of a molecule, the orientation of which is such that the molecular axis coincide with the crystal axis. The group $\mathcal{M}$ is isomorph to all the groups $\mathcal{M}(\Omega)$, and the operations ρ' of $\mathcal{M}$ are related to the corresponding operations $\rho'(\Omega)$ of $\mathcal{M}(\Omega)$ through the relation :

$$\rho' = \Omega^{-1} \rho'(\Omega) \Omega \quad \rho' \in \mathcal{M} \quad \rho'(\Omega) \in \mathcal{M}(\Omega) . \quad (2.1)$$

As proper rotations are the only operations which bring a right-handed system axis into another right-handed system axis we have to discriminate among the operations of $\mathcal{S}$ and $\mathcal{M}$ which are proper rotations and which are improper ones (i.e. inversion-rotations).

Thus, we shall write

$$\mathcal{S} = \{ e, ir_0 \} \times \mathcal{S}_r \quad (2.2a)$$

$$\mathcal{M} = \{ e, ir'_0 \} \times \mathcal{M}_r \quad (2.2b)$$

where e is the identity operation, i is the inversion, $\mathcal{S}_r$ is the reduced subgroup of $\mathcal{S}$, that is the subgroup of all proper rotations. Similar notation ($\mathcal{M}_r, ir'_0$) being used for the molecular group.

In the following, latin letters, r and r' , will be used for proper rotations only whereas Greek letters, ρ and ρ' , will be used to label symmetry operations which can be either proper or improper rotation.

We can now list the properties of the *pdf* $P_0([\Omega])$.

— *Symmetry properties related to proper rotation.*

Two orientations of the molecule which deduce one from the other through a proper rotation of the site group are by definition equally probable :

$$\forall r \in \mathcal{S}_r \quad P_0([r\Omega]) = P_0([\Omega]) . \quad (2.3)$$

Every rotation $r'(\Omega)$ of the molecular group $\mathcal{M}(\Omega)$ leaves the molecule bodily unchanged, so that the orientation of a molecule can in fact be described by any rotation of the set $\{ r'(\Omega) \Omega, r'(\Omega) \in \mathcal{M}(\Omega) \}$:

$$\forall r'(\Omega) \in \mathcal{M}(\Omega) \quad P_0([r'(\Omega) \Omega]) = P_0([\Omega]) \quad (2.4a)$$

which, in view of the relation (2.1) can be written

$$\forall r' \in \mathcal{M} \quad P_0([[\Omega]r']) = P_0([\Omega]) . \quad (2.4b)$$

— *Compatibility relation between the groups $\mathcal{S}$ and $\mathcal{M}$ and symmetry properties related to improper rotations.*

Before making explicit those properties of $P_0([\Omega])$ which are related to the improper rotations of the groups $\mathcal{S}$ and $\mathcal{M}$, it is necessary to stress that there exists a compatibility relation between these two groups : *the site group $\mathcal{S}$ cannot contain improper*

rotation if the molecular group $\mathcal{M}$ does not. Indeed, no proper rotation can bring a molecule, the point group of which does not contain improper rotations into its mirror image, whereas the existence of this mirror image is implied by the existence of improper rotations in $\mathcal{S}$.

Conversely, if the molecular group $\mathcal{M}$ contain improper rotations and the site group $\mathcal{S}$ does not, no additional properties arise for $P_0([\Omega])$. Indeed, this additional symmetry of the molecule does not affect the set of rotations describing the same physical position of the molecule. The situation is different when both groups $\mathcal{S}$ and $\mathcal{M}$ contain improper rotations. Indeed, a product such as $irir'(\Omega)$, where ir and $ir'(\Omega)$ are rotation inversions belonging respectively to the site and the molecular symmetry group, transforms a molecule with orientation Ω into an identical molecule, the orientation of which $rr'(\Omega)\Omega$ appears to be as probable as the first one. Thus $P_0([\Omega])$ fulfills the additional relation :

$$\forall ir \in \mathcal{S} \quad \forall ir'(\Omega) \in \mathcal{M}(\Omega) \quad P_0([irir'(\Omega)\Omega]) = P_0([\Omega]) \quad (2.5a)$$

which, in terms of the group $\mathcal{M}$, reads

$$\forall ir \in \mathcal{S} \quad \forall ir' \in \mathcal{M} \quad P_0([r\Omega r']) = P_0([\Omega]) \quad (2.5b)$$

2.2 THE SYMMETRY GROUP $\mathcal{F}$ OF THE pdf $P_0([\Omega])$.

2.2.1 The symmetry properties of $P_0([\Omega])$ seems to be closely related to the molecular and site symmetry group $\mathcal{S}$ and $\mathcal{M}$. Symmetry operations have a natural physical meaning when regarded as operators acting on the vectors of the usual three dimensional euclidian space; however, it is not the same when dealing with molecular orientations: improper rotation, for instance, have no meaning. Thus, we first have to define how the site and molecular symmetry operations act on functions of the molecular orientations. This will enable us to define the product group $\mathcal{SM}$ through its representation on the space of function of the Euler angles $([\Omega])$ and then to derive the actual symmetry group of $P_0([\Omega])$.

2.2.2 Let us consider the space of all the functions of the Eulerian angles $[\Omega]$. This space has a natural basis constituted by the well-known Wigner functions $D_l^{mm'}([\Omega])$ (l is an integer; m and m' take on the $2l+1$ integer values: $-l \dots +l$). These functions are the matrix elements of the irreducible representations τ_l of the full rotational group, defined on the basis of the spherical harmonics through the relation

$$[\tau_l(\Omega) Y_l^m](\theta, \varphi) = Y_l^m(\Omega^{-1}(\theta, \varphi)) = D_l^{m'm}([\Omega]) Y_l^{m'}(\theta, \varphi) \quad (2.6)$$

In particular, for any rotation r_1 and r_2 , the Wigner function verifies the following rules (see e.g. Ref. [9]) :

$$D_l^{mm'}([r_1 r_2]) = D_l^{mm'}([r_1]) D_l^{m''m'}([r_2]) \quad (2.7a)$$

and

$$D_l^{mm'}([r_1^{-1}]) = D_l^{m'm}([r_1])^* \quad (2.7b)$$

This space of functions can be considered as a representation T of a site point group $\mathcal{S}$ if we state that :

— for a proper rotation r

$$[T(r) D_l^{mm'}]([\Omega]) = D_l^{mm'}([r^{-1}\Omega]) = D_l^{m_1m}([r])^* D_l^{m_1m'}([\Omega]) \quad (2.8a)$$

— for the inversion operation

$$[T(i) D_l^{mm'}]([\Omega]) = (-1)^l D_l^{mm'}([\Omega]) \quad (2.8b)$$

Indeed, the definitions (2.8) together with the relation (2.7) ensure that the operators $T(\rho)$ verify the multiplication rule

$$\forall \rho_1, \rho_2 \in \mathcal{S} \quad T(\rho_1 \rho_2) = T(\rho_1) T(\rho_2) \quad (2.9)$$

At the same time and similarly, this space can be regarded as a representation T' of a molecular group $\mathcal{M}$ by setting :

— for a proper rotation r'

$$[T'(r') D_l^{mm'}]([\Omega]) = D_l^{mm'}([\Omega r']) = D_l^{mm_i}([\Omega]) D_l^{m_i m'}([r']) \quad (2.10a)$$

— for the inversion

$$[T'(i) D_l^{mm'}]([\Omega]) = (-1)^l D_l^{mm'}([\Omega]) \quad (2.10b)$$

According to the definitions (2.8) and (2.9), the operators $T(\rho)$ associated with the site group commute with the operators $T'(\rho')$ associated with the molecular group $(^1)$. Consequently the set of operators $\{T(\rho) T'(\rho') \mid \rho \in \mathcal{S}, \rho' \in \mathcal{M}\}$ form a group which can be regarded as the product $\mathcal{SM}$ of the site and molecular symmetry group.

2.2.3 Now, the symmetry properties (2.3), (2.4) and eventually (2.5) of the pdf $P_0([\Omega])$ appear simply as the invariance of this function under the operations of a *reduced* subgroup of $\mathcal{SM}$: the subgroup of *even* operations, that is those which involve an even number of improper rotations. In the case where both groups $\mathcal{S}$ and $\mathcal{M}$ contain improper rotation, the full symmetry group $\mathcal{F}$ of $P([\Omega])$ can thus be written under the following form

$$\mathcal{F} = \{e, ir_0 ir'_0\} \times \mathcal{S}_r \mathcal{M}_r \quad \text{with} \quad ir_0 \in \mathcal{S} \quad ir'_0 \in \mathcal{M} \quad (2.11)$$

(¹) This simply reflects that the rotations of the site group performed about the crystal axis commute with the rotations of the molecular group performed around the molecular axis. Indeed :

$$\begin{aligned} \forall \Omega \quad \rho \rho'(\Omega) &= \rho \Omega \rho' \Omega^{-1} \\ &= (\rho \Omega) \rho'(\Omega^{-1} \rho^{-1}) \rho \\ &= \rho'(\rho \Omega) \rho \end{aligned}$$

Table I. — *The symmetry group of the pdf $P_0([\Omega])$.*

$\mathcal{S} \backslash \mathcal{M}$	No improper rotation $\mathcal{M} = \mathcal{M}_r$	Improper rotation $\mathcal{M} = \{e, ir'_0\} \times \mathcal{M}_r$	
		no centred group $r'_0 \notin \mathcal{M}_r$	centred group $r'_0 \in \mathcal{M}_r$
No improper rotation $\mathcal{S} = \mathcal{S}_r$	$\mathcal{F} = \mathcal{S}_r \mathcal{M}_r = \mathcal{S} \mathcal{M}$	$\mathcal{F} = \mathcal{S}_r \mathcal{M}_r = \mathcal{S} \mathcal{M}_r$	
Improper rotation $\mathcal{S} = \{e, ir_0\} \times \mathcal{S}_r$	Impossible case	$\mathcal{F} = \mathcal{S}_r \mathcal{M}_r \times \{e, ir_0 ir'_0\}$	
			$\mathcal{F} = \mathcal{S}_r \mathcal{M}_r (*)$

(*) When $\mathcal{S}$ and $\mathcal{M}$ are both centred groups, $ir_0 ir'_0$ belongs already to $\mathcal{S}_r \mathcal{M}_r$; $\mathcal{F}$ thus reduces to $\mathcal{S}_r \mathcal{M}_r$.

which underlines the important role played by improper symmetry operations. This symmetry group has been previously derived by S. Alexander and M. Lerner Naor (Ref. [6]) as being the symmetry group of a molecular crystal Hamiltonian in this special case.

The above discussion can be summarized in table I which gives in each case the full symmetry group of the orientational probability $P_0([\Omega])$.

3. Symmetry adapted basis and development of $P_0([\Omega])$.— We now intend to develop the pdf $P_0([\Omega])$ on a set of basis functions having the same symmetry properties as $P_0([\Omega])$. We shall choose these basis functions to be independent linear combinations of Wigner functions with the same l , which belong to the identity representation of the symmetry group.

As the character of the identity representation is equal to unity for each operation, these functions could be obtained from the Wigner function by application of the projection operator

$$\Pi = \frac{1}{N} \sum_{\rho \rho' \in \mathcal{F}} T(\rho) T'(\rho')$$

where N is the number of elements of $\mathcal{F}$. However, most of the experimental data on molecular crystals are analysed with respect to the site and molecular symmetry group $\mathcal{S}$ and $\mathcal{M}$. Thus, it is useful to have a complete basis of function of $[\Omega]$ classified according to the irreducible representations of those groups. This symmetry adapted basis will be derived just below and then used to develop the orientational probability.

3.1 SYMMETRY ADAPTED FUNCTIONS. — The formulae (2.6), (2.8) and (2.10) show that the Wigner function $D_l^{mm'}([\Omega])$ transforms as the spherical harmonic Y_l^{m*} for symmetry operation of the site group and as $Y_l^{m'}$ for those of the molecular group.

For a given value of l , the space of spherical harmonics $\{Y_l^m, m = -l \dots +l\}$ can be splitted into irreducible spaces with respect to the site group $\mathcal{S}$. This decomposition leads to well-known functions, the surface harmonics relative to the point group $\mathcal{S}$ which have been derived and classified by Cracknell and Bradley (Ref. [10])

$$S_l^\lambda(\theta, \varphi) = \alpha_l^{\lambda m} Y_l^m(\theta, \varphi) \quad (3.1)$$

the label λ , which takes $2l + 1$ value, is a short hand notation for a composite index $(\Gamma \mu n)$ where :

Γ is the name of an irreducible representation of the group $\mathcal{S}$,

μ labels the independent Γ subspaces if the representation Γ is included more than once in the space $\{Y_l^m\}$,

n numbers the different basis functions for multi-dimensional Γ representations.

For a given value of l , the coefficients $\alpha_l^{\lambda m}$ form a $(2l + 1) \times (2l + 1)$ unitary matrix. The relation (2.6) can be rewritten as

$$[\tau_l(\Omega) S_l^{\lambda_1}](\theta, \varphi) = \alpha_l^{\lambda_1 m^*} D_l^{mm_1}(\Omega) \alpha_l^{\lambda_1 m_1} S_l^{\lambda_1}(\theta, \varphi). \quad (3.2)$$

From the very definition of the surface harmonics, for each rotation r of the group $\mathcal{S}$, the matrix $\alpha_l^{-1} D_l(r) \alpha_l$ is a block diagonal matrix which can be written as

$$\forall r \in \mathcal{S} \quad \alpha_l^{\lambda m^*} D_l^{mm_1}(r) \alpha_l^{\lambda_1 m_1} = \delta_{\Gamma \Gamma_1} \delta_{\mu \mu_1} M_{\Gamma}^{m m_1}(r) \quad (3.3)$$

where $\lambda = \Gamma, \mu, n$, $\lambda_1 = \Gamma_1, \mu_1, n_1$ and $M_{\Gamma}^{m m_1}$ is the matrix of the Γ representation of $\mathcal{S}$.

In the same way, the space $\{Y_l^m\}$ can be splitted into irreducible subspaces with respect to the mole-

cular group $\mathcal{M}$, this leads to the surface harmonics relative to $\mathcal{M}$

$$M_l^{\lambda'}(\theta, \varphi) = \beta_l^{\lambda'm'} Y_l^{m'}(\theta, \varphi) \quad (3.4)$$

where λ' is a composite index (Γ', μ', n') with notations analogous to the above ones.

For a given l , the unitary matrix $\alpha_l^{\lambda'm}$ and $\beta_l^{\lambda'm'}$ appearing in (3.1) and (3.4) are used to set up a new basis for functions of $[\Omega]$

$$\Delta_l^{\lambda\lambda'}([\Omega]) = \alpha_l^{\lambda m*} \beta_l^{\lambda' m'} D_l^{mm'}([\Omega]) \quad (3.5)$$

the interest of this transformation is that, as Wigner matrices transform as the spherical harmonics, a direct application of ((2.8), (2.9) and (3.3)) shows that an operation $T(\rho) T'(\rho')$ associated with the product group $\mathcal{S}\mathcal{M}$ transforms the basis functions $\Delta_l^{\lambda\lambda'}$ according to the representation $\Gamma^* \Gamma'$ of the group $\mathcal{S}\mathcal{M}$. (Γ and Γ' are respectively the irreducible representations of $\mathcal{S}$ and $\mathcal{M}$ which are understood in the index λ and λ' , and Γ^* is the representation conjugate to the representation Γ .) For brevity, we shall say that $\Delta_l^{\lambda\lambda'}([\Omega])$ is in the Γ representation of $\mathcal{S}$ and in the Γ' representation of $\mathcal{M}$.

Remark. — When the groups $\mathcal{S}$ and $\mathcal{M}$ are not both centred groups, the product $\mathcal{S}\mathcal{M}$ is a direct product group (i.e. every element of the product $\mathcal{S}\mathcal{M}$ can be represented in a unique way as the product $T(\rho) T'(\rho')$ where ρ belongs to $\mathcal{S}$ and ρ' to $\mathcal{M}$). In that case, the irreducible representations of the product $\mathcal{S}\mathcal{M}$ are all the possible products of the irreducible representations of $\mathcal{S}$ and $\mathcal{M}$ respectively (cf. Ref. [11]). This is no longer true when $\mathcal{S}$ and $\mathcal{M}$ are both centred groups. Indeed, in that case, each element of $\mathcal{S}\mathcal{M}$ can be represented in two ways as $T(\rho) T'(\rho')$ or as $T(i\rho) T'(i\rho')$. A centred group is itself a direct product of its reduced subgroup of proper rotations with the group $\mathfrak{I} = \{e, i\}$. The irreducible representations of such a group fall into two categories : the even « g » representation generated by the identity representation of $\mathfrak{I}$ and the odd « u » representation generated by the other representation of $\mathfrak{I}$. One can show that the irreducible representations of $\mathcal{S}\mathcal{M}$ are the products $\Gamma_g \Gamma'_g$ or $\Gamma_u \Gamma'_u$ of representations of $\mathcal{S}$ and $\mathcal{M}$ which have the same parity with respect to inversion operation. In fact, the mixed products $\Gamma_u \Gamma'_g$ or $\Gamma_g \Gamma'_u$ are not representations of $\mathcal{S}\mathcal{M}$ because they associate two different operators (for instance $\Gamma_u(\rho) \Gamma'_g(\rho')$ and $\Gamma_u(i\rho) \Gamma'_g(i\rho') = -\Gamma_u(\rho) \Gamma'_g(\rho')$) with the two ways of writing the same element of $\mathcal{S}\mathcal{M}$. As the space generated by the manifold $D_l^{mm'}([\Omega])$ is a representation of $\mathcal{S}\mathcal{M}$, those mixed products cannot appear in its decomposition into irreducible subspaces $\Delta_l^{\lambda\lambda'}([\Omega])$.

3.2 DEVELOPMENT OF THE ORIENTATIONAL PROBABILITY $P_0([\Omega])$.

— The basis functions $\Delta_l^{\lambda\lambda'}$ derived in part 3.1 can be

used to develop the probability $P_0([\Omega])$

$$P_0([\Omega]) = \sum_{l\lambda\lambda'} A_l^{\lambda\lambda'} \Delta_l^{\lambda\lambda'}([\Omega]) \quad (3.6)$$

The basis functions $\Delta_l^{\lambda\lambda'}$ transform according to the irreducible representations of the product $\mathcal{S}\mathcal{M}$, while the symmetry group $\mathfrak{F}$ of $\mathfrak{P}([\Omega])$ is only the *reduced* subgroup of $\mathcal{S}\mathcal{M}$. To eliminate from this development all the trivial and redundant coefficients we have to derive, in each case, which representations of $\mathcal{S}\mathcal{M}$ induce the unity representation of $\mathfrak{F}$. This problem may be simplified by the following remark.

In any case, the group $\mathfrak{F}$ includes as a subgroup the direct product $\mathcal{S}_r \mathcal{M}_r$. Thus, the representation of $\mathcal{S}\mathcal{M}$ which are allowed in the development of $P_0([\Omega])$ must be searched among those which induce the unity representation of $\mathcal{S}_r \mathcal{M}_r$.

In the following, we shall call Γ_0 and Γ'_0 the unity representations of the reduced groups $\mathcal{S}_r$ and $\mathcal{M}_r$. The unity representations of $\mathcal{S}_r \mathcal{M}_r$ is thus the product $\Gamma_0 \Gamma'_0$. For a point group $\mathcal{S}$ containing improper rotation, one can prove that there is two one-dimensional representations of that group which induce the unity representation of its reduced subgroup. The first one, we shall note Γ_0^+ is the unity representation of $\mathcal{S}$ while the other one, we shall note Γ_0^- , has no special name except in the case of a centred group where it is the odd representation (A_{1u}). The characters of those two representations are general and given in table II. The same consideration is valid if the molecular group $\mathcal{M}$ contains improper rotations and we shall call $\Gamma_0'^+$ and $\Gamma_0'^-$ the two representations of $\mathcal{M}$ inducing the identity representation Γ'_0 of $\mathcal{M}_r$. We can now, for the different case of table I, list the representations of $\mathcal{S}\mathcal{M}$ which induce the identity representation of $\mathfrak{F}$.

Table II. — *Characters of the two representations of a point group $\mathcal{S}$ (containing improper rotations) which induce the identity representation of the reduced subgroup $\mathcal{S}_r$.*

	$r \in \mathcal{S}_r$	$ir \in \mathcal{S}$
	—	—
Γ_0^+	+ 1	+ 1
Γ_0^-	+ 1	− 1

In the first case where both symmetry groups $\mathcal{M}$ and $\mathcal{S}$ are purely rotational group, the only allowed representation of $\mathcal{S}\mathcal{M}$ is the product $\Gamma_0 \Gamma'_0$ of the unity representation of $\mathcal{S}$ and $\mathcal{M}$. The development of $P_0([\Omega])$ thus reduces to :

$$P_0([\Omega]) = \sum_{\substack{l\lambda_0\lambda'_0 \\ \lambda_0 \in \Gamma_0 \\ \lambda'_0 \in \Gamma'_0}} A_l^{\lambda_0\lambda'_0} \Delta_l^{\lambda_0\lambda'_0}([\Omega]) \quad (3.7)$$

In the second case, where the molecular group $\mathcal{M}$ contains improper rotations while the site group $\mathcal{S}$

does not, the two possible products $\Gamma_0 \Gamma_0'^+$ and $\Gamma_0 \Gamma_0'^-$ generate the unity representation of $\mathcal{S}$ and the development of $P_0([\Omega])$ can be written

$$P_0([\Omega]) = \sum_{\substack{l\lambda_0\lambda_0'^+ \\ \lambda_0 \in \Gamma_0 \\ \lambda_0'^+ \in \Gamma_0'^+}} A_l^{\lambda_0\lambda_0'^+} A_l^{\lambda_0\lambda_0'^+}([\Omega]) + \sum_{\substack{l\lambda_0\lambda_0'^- \\ \lambda_0 \in \Gamma_0 \\ \lambda_0'^- \in \Gamma_0'^-}} A_l^{\lambda_0\lambda_0'^-} A_l^{\lambda_0\lambda_0'^-}([\Omega]) . \quad (3.8)$$

Remark. — If $\mathcal{M}$ is a centred group, the identity representation A_{1g} of $\mathcal{M}$ is included only in the manifolds $\{Y_l^m\}$ with an even value of l , while the odd representation A_{1u} can occur only for an odd value of l . Consequently, the development (3.8) includes only functions of the first kind $A_l^{\lambda_0\lambda_0'^+}$ for even values of l , and functions of the second kind $A_l^{\lambda_0\lambda_0'^-}$ for odd values of l . This remark is not valid for a molecular group which is not a centred group. For instance, the representation A_2 of the tetrahedral group $T_d(\Gamma_0^- = A_2)$, is included in the manifolds $l=6, 9, 10, 12$ etc... while A_1 ($A_1 = \Gamma_0'^+$) is included in the manifolds

$$l = 0, 3, 4, 6, 7, 8, 9, \text{ etc...}$$

At last, when both symmetry groups contain improper rotations, the allowed representations for $P_0([\Omega])$ must be searched among the four products $\Gamma_0^+ \Gamma_0'^+$, $\Gamma_0^- \Gamma_0'^+$, $\Gamma_0^+ \Gamma_0'^-$ and $\Gamma_0^- \Gamma_0'^-$. It is clear, from table II, that only $\Gamma_0^+ \Gamma_0'^+$ and $\Gamma_0^- \Gamma_0'^-$ generate the unity representation of $\mathcal{S}$. According to the remark at the end of part (3.1), this result holds even in the case when both groups $\mathcal{S}$ and $\mathcal{M}$ are centred groups. Thus the development of $P_0([\Omega])$ appears to be :

$$P_0([\Omega]) = \sum_{\substack{l\lambda_0\lambda_0'^+ \\ \lambda_0 \in \Gamma_0^+ \\ \lambda_0'^+ \in \Gamma_0'^+}} A_l^{\lambda_0\lambda_0'^+} A_l^{\lambda_0\lambda_0'^+}([\Omega]) + \sum_{\substack{l\lambda_0\lambda_0'^- \\ \lambda_0 \in \Gamma_0^- \\ \lambda_0'^- \in \Gamma_0'^-}} A_l^{\lambda_0\lambda_0'^-} A_l^{\lambda_0\lambda_0'^-}([\Omega]) . \quad (3.9)$$

Remark. — If $\mathcal{S}$ and $\mathcal{M}$ are both centred groups, functions of the first kind $A_l^{\lambda_0\lambda_0'^+}$ appear only for even values of l while functions of the second kind appear for odd values of l .

3.3 CONCLUSION. — The above method provides in every case a complete and non redundant set of basis functions which fulfills the symmetry properties of the *pdf* $P_0([\Omega])$. It must be stressed that in the case of symmetry groups containing improper rotations, the development of $P_0([\Omega])$ involves basis functions which are not in the unity representation of the molecular and site symmetry groups. In that case, the symmetry adapted functions for $P_0([\Omega])$ falls into two categories : those which are related with the

unity representation Γ_0^+ and $\Gamma_0'^+$ of the groups $\mathcal{S}$ and $\mathcal{M}$ and those which are related to the other allowed representations of these groups Γ_0^- and $\Gamma_0'^-$.

The results presented here are not completely new. Hüller and Press (Ref. [12]) have already used those symmetry adapted functions to develop the probability $P_0([\Omega])$ and calculate the coherent elastic scattering function of a disordered molecular crystal. However these authors used an incomplete basis including only the functions related to the identity representations of the molecular and site groups. Nevertheless, their results are correct and the reason for this is quite simple and general.

In most cases, informations about the orientational structure of disordered molecular crystals are derived from the measures of a molecular observable. In crystal axes, the value of this observable depends on the molecular orientation with respect to the crystal axis and experimental data correspond to an averaging over all molecular orientations. As this observable is, by definition, in the unity representation of the molecular group the measured mean value is only related to those coefficients of $P_0([\Omega])$ which are in the unity representation of $\mathcal{M}$ and therefore of $\mathcal{SM}$.

However, we shall see in the next paper, that the coefficients of the second kind (related to the representation Γ_0^- and $\Gamma_0'^-$) have a real physical meaning and that they can in principle be measured through incoherent neutron scattering experiments.

4. Examples. — Three examples will now illustrate the above formalism. In the first one, a tetrahedral molecule ($\mathcal{M} = T_d$) is placed in a cubic site ($\mathcal{S} = O_h$). This is the case of the high temperature phases of CD_4 , CBr_4 and neopentane $C(CH_3)_4$. The two other examples correspond to the two disordered phases of tertibutyl-chlorine $CCl(CH_3)_3$. The molecular group is C_{3v} and the site group is O_h in the high temperature phase or D_{4h} below the transition temperature. In each case, we shall give for the first values of the index l the number of independent symmetry adapted functions which appears in the development of the *pdf* $P_0([\Omega])$. We shall adopt the crystallographic notations for the irreducible representations of the groups T_d , C_{3v} , O_h and D_{4h} . Thus, for instance, the five representations of T_d are noted A_1 , A_2 , E , F_1 and F_2 and we can easily identify the identity representation $\Gamma_0'^+ = A_1$ and the other allowed representation $\Gamma_0'^- = A_2$.

The first step consists in splitting the space

$$\{Y_l^m \quad m = -l \dots +l\}$$

into irreducible subspaces with respect to the four groups T_d , C_{3v} , O_h and D_{4h} . For the first values of l , this decomposition can be found in reference [10], from which one easily writes down table III.

Now we just have to count, for each value of l , the number of possible products $\Gamma_0^+ \Gamma_0'^+$ and $\Gamma_0^- \Gamma_0'^-$. The results corresponding to each one of the three cases we have consider appears below in table IV.

Table III. — *Decomposition into irreducible subspaces of the first l manifolds.*

	T_d	C_{3v}	O_h	D_{4h}
$l = 0$	A_1	A_1	A_{1g}	A_{1g}
$l = 1$	F_2	$A_1 + E$	F_{1u}	$A_{2u} + E_u$
$l = 2$	$E + F_2$	$A_1 + 2E$	$E_g + F_{2g}$	$A_{1g} + B_{1g} + B_{2g} + E_g$
$l = 3$	$A_1 + F_2 + F_1$	$2A_1 + A_2 + 2E$	$A_{2u} + F_{1u} + F_{2u}$	$A_{2u} + B_{1u} + B_{2u} + 2E_u$
$l = 4$	$A_1 + E + F_2 + F_1$	$2A_1 + A_2 + 3E$	$A_{1g} + E_g + F_{1g} + F_{2g}$	$2A_{1g} + A_{2g} + B_{1g} + B_{2g} + 2E_g$
$l = 5$	$E + 2F_2 + F_1$	$2A_1 + A_2 + 4E$	$E_u + 2F_{1u} + F_{2u}$	$A_{1u} + 2A_{2u} + B_{1u} + B_{2u} + 3E_u$
$l = 6$	$A_1 + A_2 + E + 2F_2 + F_1$	$3A_1 + 2A_2 + 4E$	$A_{1g} + A_{2g} + E_g + 2F_{2g} + F_{1g}$	$2A_{1g} + A_{2g} + 2B_{1g} + 2B_{2g} + 3E_g$
$l = 7$	$A_1 + E + 2F_2 + 2F_1$	$3A_1 + 2A_2 + 5E$	$A_{2u} + E_u + 2F_{1u} + 2F_{2u}$	$A_{1u} + 2A_{2u} + 2B_{1u} + 2B_{2u} + 4E_u$
$l = 8$	$A_1 + 2E + 2F_2 + 2F_1$	$3A_1 + 2A_2 + 6E$	$A_{1g} + 2E_g + 2F_{2g} + 2F_{1g}$	$3A_{1g} + 2A_{2g} + 2B_{1g} + 2B_{2g} + 4E_g$
$l = 9$	$A_1 + A_2 + E + 2F_1 + 3F_2$	$4A_1 + 3A_2 + 6E$	$A_{1u} + A_{2u} + E_u + 3F_{1u} + 2F_{2u}$	$2A_{1u} + 3A_{2u} + 2B_{1u} + 2B_{2u} + 5E_u$

Table IV. — *Number of independent, non trivial coefficient in the development of the pdf $P_0(|\Omega|)$.*

$j \backslash S.M.$	$O_h T_d$		$O_h C_{3v}$		$D_{4h} C_{3v}$	
	$A_{1g} A_1$	$A_{1u} A_2$	$A_{1g} A_1$	$A_{1u} A_2$	$A_{1g} A_1$	$A_{1u} A_2$
0	1		1		1	
1						
2					1	
3						
4	1		2		4	
5						1
6	1		3		6	
7						2
8	1		3		9	
9		1		3		6

The basis functions for $l = 0$ correspond to a uniform density of orientational probability. The coefficient of this function in $P_0(|\Omega|)$ is always equal to unity, which ensures that $P_0(|\Omega|)$ is normalized. Thus, for a tetrahedral molecule in a cubic site, the first non trivial coefficient of $P_0(|\Omega|)$ arises for $l = 4$,

and the first coefficient which is not in the identity representation of O_h and T_d must be waited until $l = 9$. This is due to the high symmetry of this case. For a molecule C_{2v} in a site C_{2v} , for instance, coefficients of the second kind arise for $l = 2, 3, 4, 5 \dots$ etc. Tables of reference [10] give also the coefficients α_l^{im} and $\beta_l^{i'm'}$ which related surface harmonics to spherical harmonics. They can be used to explicit symmetry adapted functions according to formula (3.3).

Remark. — The above formalism can also be applied to the simple case of a linear molecule. Then, the molecular symmetry group is $\mathcal{D}_{\infty h}$ if the molecule has a symmetry centre (a dumb-bell molecule for instance) and $C_{\infty v}$ otherwise.

Let us choose the molecular axis $\{x, y, z\}$ in such a way that the z axis is the C_{∞} axis of the molecule.

For a given orientation of the molecule characterized by the Euler angles $[\Omega] = (\theta, \varphi, \psi)$, the spherical coordinates (Θ, Φ) of the C_{∞} axis in the crystal axis are :

$$\begin{cases} \Theta = \theta \\ \Phi = \psi - \pi/2 \end{cases} \tag{4.1}$$

the surface harmonics which are in the identity representation of C_{∞} are just the spherical harmonics Y_l^0 ;

Y_l^0 is in the identity representation of $C_{\infty v}$;
 Y_l^0 is in the identity representation of $\mathcal{D}_{\infty h}$ for l even, and in the A_{1u} representation of $\mathcal{D}_{\infty h}$ for l odd.

Thus, the symmetry adapted function for the *pdf* $P_0([\Omega])$ are the following :

$$\Delta_l^{i'o}([\theta, \varphi, \psi]) = \alpha_l^{i'm*} D_l^{m_o}(\theta, \varphi, \psi) . \quad (4.2)$$

From the relations given in reference [9], one easily show that

$$D_l^{m_o}(\theta, \varphi, \psi) = Y_l^{m*}(\Theta, \Phi) \sqrt{\frac{4\pi}{2l+1}} . \quad (4.3)$$

In the case of linear molecule, one recovers symmetry adapted functions which, of course, only depend on the spherical coordinate of the molecular axis and which are just the surface harmonics relative to the site group S as it was expected.

5. Conclusion. — The formalism developed here provides a complete and orthonormal set of basis functions $\Delta_l^{i'i'}([\Omega])$ suitable for the description of orientationally disordered molecular crystals. Those basis functions can be called *symmetry adapted functions* as they transform, at the same time, according to the irreducible representations of both the site symmetry group S and the molecular symmetry group $\mathcal{M}$. The development of the orientational probability density functions $P_0([\Omega])$ on such a basis provides a set of independent parameters which characterize the mean long range order of plastic phases. In the same way, the canonical basis could be used to analyse any function of the molecular orienta-

tions, such as the mean potentiel $V([\Omega])$ experienced by one molecule in the surrounding of the others. In the following papers, we shall use this basis to describe the dynamics of molecular reorientations and analyse the experimental data arising from neutron, Raman and infrared scattering experiment.

In this paper, the orientational *pdf* has been defined independently from the instantaneous position of the molecular centre of mass which is assumed to be in its equilibrium position. Recently, Hüller, Press and Grimm (Ref. [13]) have extended the method of symmetry adapted functions to the development of conditional *pdf* $P_0([\Omega], \mathbf{R})$ in order to take into account the correlation between the orientational *pdf* and the instantaneous position of the molecular centre of mass, $\mathbf{R}$.

The main originality of this paper lies on the close study of the symmetry problems encountered when a molecule with a point group symmetry $\mathcal{M}$ is located on a site with a point group symmetry S . When both the molecular and site groups involve improper rotations, the full symmetry group of the orientational probability function $P_0([\Omega])$ is only the *reduced* subgroup $(S\mathcal{M})_r$ of all proper rotations included in the product $S\mathcal{M}$. Thus, in that case, the development of $P_0([\Omega])$ involves basis functions which are not generally considered because they are not in the identity representation of $S\mathcal{M}$. However, we shall see in a next paper that the associated coefficients are crystal observables and arise directly, for instance, in the analysis of incoherent neutron scattering data.

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