

***J*-ferroics: A rotational-invariant classification of structural phase transitions**

D. Paquet and J. Jerphagnon

PECIRPM, Centre National d'Etudes des Télécommunications, 196 rue de Paris, 92220 Bagneux, France*

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Rotational-invariance considerations are applied to structural phase transitions. A new classification in accordance with the onset of the spontaneous irreducible tensors in the ferroic phase is proposed for nonmagnetic ferroic materials. This classification gives an intrinsic description of any ferroic domain structure. It also allows easy specification of the spontaneous extensive quantities, the spontaneous response functions, and the switching processes associated with each ferroic species, thus paving the bridge between the different classifications in the literature.

I. INTRODUCTION

The concept of ferroicity, although recently introduced, embodies a wide range of physical phenomena known for a long time, spreading from the magnetic properties of iron to the phenomenon of quartz detwinning.

Through the years there has been a shift in the meaning of the prefix *ferro* which is now used to describe different material properties in a somewhat confused manner. Ferromagnetism originally designated the properties of materials which, like iron, cobalt, or nickel, have a high magnetic permeability. Since in these materials there exists, in the absence of any magnetic field, a spontaneous magnetization M_s , which vanishes at the Curie temperature, ferromagnetism often refers to the fact that the low-temperature phase contains two or more regions, called domains, corresponding to different orientations of M_s . A third meaning of *ferro* is associated with the fact that these domains can be switched from one to the other by application of a magnetic field. Indeed the special feature of a ferroic material is the existence of a domain structure which customarily originates from a phase transition. The macroscopic physical properties of a given domain depends on its orientation which can be changed by application of external forces.

According to the above considerations, Aizu^{1,2} defined a ferroic as a crystal which possesses, in the absence of any applied magnetic (H), electric (E), or stress (σ) fields two or more orientation states, and can be shifted from one to another of these states by application of one (or a combination) of these external forces. More recently, following these ideas, Newnham and Cross^{3,4} illustrated by specific examples the notions of primary, secondary, and higher-order ferroics: if the difference in Gibbs potential between two different domains of a ferroic is expanded in powers of the applied external forces (H, E, σ), the order of ferroicity is that of the lowest degree

homogeneous polynomial in H, E, σ appearing in this expansion. Primary ferroics are ferromagnets (H), ferroelectrics (E), and ferroelastics (σ). Secondary ferroics are ferrobielectrics (E^2), ferrobimagnetics (H^2), ferrobielastics (σ^2), ferromagnetoelastics (HE), ferromagnetoelastics ($H\sigma$), and ferroelastoelectrics (σE). We shall call this classification the "switching force classification."

Using a different approach, Konak *et al.*⁵ emphasized the fact that some response-function tensors (gyration, piezoelectricity, ..., tensors) differ from one domain to another. This enables to evidence a given domain structure by macroscopic experiments. These authors sketched out the "response-function classification" based on the physical nature of the response functions which differ between domains.

However, another natural classification appears: The domain structure of a ferroic generally originates from a phase transition between a high-symmetry "prototypic" phase and one of lower symmetry called "ferroic" which can be characterized by the spontaneous extensive quantities appearing at the transition and differing in orientation between domains. Well-known examples are ferromagnets, ferroelectrics, and ferroelastics associated, respectively, with a spontaneous magnetization, a spontaneous polarization, and a spontaneous strain. To our knowledge, no generalization of such a classification has been proposed for all ferroic species.

Until now, no one-to-one correspondence has been established between these three classifications (namely, switching forces, response functions, and spontaneous extensive quantities). Furthermore, for a given ferroic species several types of driving forces can be used to switch the domains. In that respect, is there really a difference between ferroelastic and ferrobielectric materials? Is there a specific spontaneous extensive quantity associated with ferroelastoelectrics? Is spontaneous optical activity associated with the onset of a specific spontaneous extensive quantity or switching process? One is therefore led, in trying

to build up a general classification of phase transitions, to refer to intrinsic properties of the material, and to consider the onset of new tensorial properties t_i in the ferroic phase as compared with the prototypic phase, whatever those physical properties may be. For instance ferroelasticity corresponds to the onset of a second-rank tensor, describing either the spontaneous strain, or the spontaneous birefringence. More precisely, the symmetric second-rank tensor involved in this case is traceless, i.e., an irreducible second-rank tensor (a so-called deviator). Due to the fact that the minimum common supergroup of all crystallographic point groups is the whole rotation-inversion group O_3 , and that the intrinsic properties of any material are independent of the orientation of the reference frame relative to which they are observed, we will now emphasize the rotational-invariance properties of the spontaneous tensors, and thus pay attention to their decomposition into irreducible spherical tensors.⁶

It is the purpose of this paper to generalize all the former classifications of ferroic materials by introducing the J -ferroic classification according to the lowest weight J of the irreducible spontaneous spherical tensors appearing in the ferroic phase, and vanishing by symmetry in the prototypic phase. The polar or axial character of the spontaneous tensors will be related to the onset of spontaneous extensive quantities (polarization, strain,...) and of spontaneous response functions (pyroelectricity, birefringence, optical activity,...). After tabulating for each ferroic species their associated spontaneous spherical tensors, the J -ferroic classification will be related to those of Aizu and of Konak *et al.* The switching and domain properties will be discussed.

Note that the structural phase transitions considered are those concomitant with a change in the macroscopic properties of the material which implies a change in the point-group symmetry. Structural phase transitions involving changes only in the translational symmetry are not dealt with in this paper. There will therefore be no consideration of the anti-phase domains⁷ nor distinction between proper and improper ferroics. These topics have been considered in the work of Toledano and Toledano,⁸ who presented an extensive discussion of the ferroic phase transitions in terms of symmetry properties of the order parameter, thus taking account of the possible changes in the translational symmetry. In addition we shall restrict our considerations to the case of nonmagnetic materials and properties.

II. DEFINITION OF J -FERROICS

Let us consider a ferroic crystal with a given domain structure. Each domain possesses a certain point-group symmetry G_f . S is a symmetry operation

of O_3 which does not belong to G_f , but transforms one domain into another. The set of all S , together with all operations of G_f , generates a point group G_p called the point group of the prototypic phase. The notion of prototypic phase thus exists even in the absence of any effective phase transition for the ferroic material, and corresponds to ferroic symmetry averaged over all the possible orientations of the domains. Any operation S belonging to G_p but not to G_f transforms the spontaneous tensorial quantities t in the following way:

$$t_k = S(t_i)$$

if S transforms domain i into domain k .

Any Cartesian tensor t can be split into irreducible spherical tensors⁶ $t^{J,\epsilon}$ belonging to the $2J+1$ dimensional irreducible representation D_f^J of O_3 . J is called the weight of the spherical tensor, and ϵ its parity. Irreducible tensors of weight J are either polar [parity $(-1)^J$] or axial [parity $(-1)^{J+1}$]. If one splits any spontaneous tensor into irreducible spherical components $t^{J,\epsilon}$, one obtains the following transformation equations:

$$t_k^{J,\epsilon} = S(t_i^{J,\epsilon})$$

while $t_k^{J,\epsilon} = R(t_i^{J,\epsilon})$ if R belongs to G_f . This shows that spontaneous irreducible spherical tensors are characteristics of a given species, i.e., of a given couple (G_p, G_f) .

We thus define a J -ferroic as a ferroic whose lowest-weight spontaneous irreducible spherical tensor is of weight J . For each value of J a distinction has to be made between J (polar)- and pseudo- J (axial)-ferroics. By definition there is no scalar ferroic ($J=0^+$ implies no difference between G_p and G_f). On the contrary, pseudoscalar ferroics ($J=0^-$) exist. $J=1^-$ and 2^+ ferroics correspond, respectively, to ferroelectrics and pure ferroelastics.

III. DETERMINATION OF THE SPHERICAL TENSORS ASSOCIATED TO A GIVEN FERROIC SPECIES

The whole set of spontaneous spherical tensors associated with a given ferroic species can be easily found using the following remarks:

(i) The prototypic phase belongs to a point symmetry associated with a subgroup of O_3 . Thus each irreducible representation (IR) $D^{J,\epsilon}$ splits into one or several IR of the prototypic point group.

(ii) Each IR of the prototypic point group splits into one or several IR of the ferroic point group.

(iii) Any spontaneous spherical tensor is invariant under application of any symmetry operation of G_f , but is changed by application of at least one operation of G_p . Thus the spontaneous spherical tensors transform like the $D^{J,\epsilon}$ which split into at least one not-totally-symmetric IR of G_p containing the trivial IR of G_f .

The 32 crystallographic point groups are subgroups of either $m\bar{3}m$ or $6/mmm$, which, respectively, possess 10 and 12 different IR (discarding the double-group ones). Due to this finite number of different IR, a maximum weight exists, such that any spherical tensor of greater weight splits into several IR already found in the decomposition of some spherical tensor of lower weight. This maximum weight appears to be 3 if one discards the parity of the spherical tensors, and 9 if one is restricted to polar tensors.

Thus to specify any ferroic species, one has to list only the set of spontaneous spherical tensors (respectively, polar spontaneous spherical tensors) up to weight 3 (respectively, 9), as done in Table I: with each ferroic species are associated (i) the weight J of the spontaneous polar spherical tensors and (ii) the weight J of the spontaneous axial spherical tensors.

For the sake of simplicity, we have only listed maximal ferroic species, i.e. species such that any su-

perpoint group of the ferroic point group contains the prototype point group. Whenever one must determine the spontaneous spherical tensors associated with a nonmaximal species, one follows the different paths through maximal species leading from the prototypic to the ferroic point groups. The spontaneous spherical tensors are those appearing along any one of these paths.

For instance, the room-temperature ferroic structure of $Ba_2NaNb_5O_{15}$ corresponds to the species $4/mmmFmm2$; three paths appear:

$$4/mmm \rightarrow \bar{4}2m \rightarrow mm2 \quad .$$

$$4/mmm \rightarrow mmm \rightarrow mm2 \quad .$$

$$4/mmm \rightarrow 4mm \rightarrow mm2 \quad .$$

It is easily verified that the same spontaneous tensors appear along any of the filiations: $1^-, 2^+, 3^-$ and $2^-, 3^+$.

TABLE I. Spontaneous irreducible spherical tensors associated with each maximum ferroic species.

Prototypic phase	Maximum ferroic phase	Polar spontaneous spherical tensor	Axial spontaneous spherical tensor	Lowest-order switching force
$m\bar{3}m$	$m\bar{3}$	6^+	3^+	$\sigma^3, \sigma E^2$
	432	9^-	$0^-, 4^-$	$\sigma^2 E$
	$\bar{4}3m$	3^-	\dots	σE
	$\bar{3}m$	2^+	3^+	σ
	$4/mmm$	2^+	\dots	σ
$m\bar{3}$	23	3^-	$0^-, 4^-$	σE
	$\bar{3}$	2^+	$1^+, 3^+$	σ
	mmm	2^+	\dots	σ
432	23	3^-	3^+	σE
	$\bar{4}2m$	2^+	2^-	σ
	$3m$	1^-2^+	3^+	E, σ
$\bar{4}3m$	$\bar{4}2m$	2^+	2^-	σ
	23	6^+	$0^-3^+4^-$	$\sigma^3, \sigma E^2, \sigma^2 E$
	$3m$	1^-2^+	3^+	E, σ
23	222	2^+	2^-	σ
	3	1^-2^+	$1^+2^-3^+$	E, σ
$6/mmm$	622	7^-	$0^-2^-4^-$	σE
	$6/m$	6^+	$1^+, 3^+$	$\sigma^3, \sigma E^2$
	$\bar{3}m$	4^+	3^+	σ^2
	$\bar{6}2m$	3^-	4^-	σE
	mmm	2^+	3^+	σ
622	$6mm$	1^-3^-	4^-	E
	222	2^+	2^-	σ
	6	1^-	1^+3^+	E
	32	3^-4^+	3^+	$\sigma E, \sigma^2$
	$6/m$	$\bar{3}$	4^+	3^+
$6/m$	$\bar{6}$	3^-	4^-	σE
	$2/m$	2^+	3^+	σ
	6	1^-	0^-2^-	E
6mm	6	6^+	$0^-1^+2^-3^+4^-$	σE
	$3m$	3^-4^+	3^+	$\sigma E, \sigma^2$
	$mm2$	2^+	2^-3^+	σ

TABLE I. (continued)

Prototypic phase	Maximum ferroic phase	Polar spontaneous spherical tensor	Axial spontaneous spherical tensor	Lowest-order switching force
$\bar{6}m2$	32	4 ⁺	0 ⁻²⁻³⁺	$\sigma E, \sigma^2$
	$\bar{6}$	3 ⁻	1 ⁺³⁺⁴⁻	σE
	3m	1 ⁻	3 ⁺	E
	mm2	1 ⁻²⁺	2 ⁻³⁺	E, σ
6	3	3 ⁻ , 4 ⁺	3 ⁺⁴⁻	$\sigma E, \sigma^2$
	2	2 ⁺	2 ⁻³⁺	σ
$\bar{6}$	m	1 ⁻²⁺	2 ⁻³⁺	σ, E
	3	1 ⁻³⁻	0 ⁻²⁻³⁺	E
4/mmm	422	5 ⁻	0 ⁻²⁻⁴⁻	σE
	4/m	4 ⁺	1 ⁺³⁺	σ^2
	$\bar{4}2m$	3 ⁻	2 ⁻	σE
	mmm	2 ⁺	3 ⁺	σ
	4mm	1 ⁻	...	E
4/m	$\bar{4}$	3 ⁻	2 ⁻	σE
	2/m	2 ⁺	3 ⁺	σ
	4	1 ⁻	0 ⁻²⁻	E
422	222	2 ⁺	2 ⁻³⁺	σ
	4	1 ⁻	1 ⁺³⁺	E
$\bar{4}2m$	$\bar{4}$	3 ⁻⁴⁺	1 ⁺²⁻³⁺	$\sigma E, \sigma^2$
	222	2 ⁺	0 ⁻²⁻³⁺	σ
	mm2	1 ⁻²⁺	3 ⁺	σ, E
4mm	4	4 ⁺	0 ⁻¹⁺²⁻³⁺	$\sigma^2, \sigma E$
	mm2	2 ⁺	2 ⁻³⁺	σ
$\bar{4}$	2	1 ⁻²⁺	0 ⁻²⁻³⁺	E, σ
4	2	2 ⁺	2 ⁻³⁺	σ
	32	1 ⁻²⁺	1 ⁺²⁻³⁺	σ, E
3m	3	1 ⁻	1 ⁺³⁺	E
	m	1 ⁻²⁺	1 ⁺²⁻³⁺	E, σ
$\bar{3}m$	3	3 ⁻⁴⁺	0 ⁻¹⁺²⁻³⁺	$\sigma E, \sigma^2$
	$\bar{3}$	4 ⁺	1 ⁺³⁺	σ^2
$\bar{3}$	32	3 ⁻	0 ⁻²⁻	σE
	2/m	2 ⁺	1 ⁺³⁺	σ
	3m	1 ⁻³⁻	...	E
$\bar{3}$	$\bar{1}$	2 ⁺	1 ⁺³⁺	σ
	3	1 ⁻	0 ⁻²⁻	E
3	1	1 ⁻²⁺	1 ⁺²⁻³⁺	σ, E
mmm	222	3 ⁻	0 ⁻²⁻	σE
	2/m	2 ⁺	1 ⁺³⁺	σ
	mm2	1 ⁻	...	E
222	2	1 ⁻²⁺	1 ⁺²⁻³⁺	σ
mm2	2	2 ⁺	0 ⁻¹⁺³⁺	σ
	m	1 ⁻²⁺	1 ⁺²⁻³⁺	E, σ
2/m	$\bar{1}$	2 ⁺	1 ⁺³⁺	σ
	2	1 ⁻	0 ⁻²⁻	E
	m	1 ⁻²⁺	2 ⁻	σ, E
2	1	1 ⁻²⁺	1 ⁺²⁻³⁺	σ, E
m	1	1 ⁻²⁺	1 ⁺²⁻³⁺	σ, E
$\bar{1}$	1	1 ⁻	0 ⁻²⁻	E

IV. RELATION WITH THE OTHER CLASSIFICATIONS

A. Spontaneous extensive quantities

Since magnetic properties are disregarded, all the spontaneous extensive quantities correspond with electric n poles which describe, from a macroscopic point of view, the change occurring in the charge distribution inside the crystal at the transition between the prototypic and the ferroic phases. Such n poles transform like polar spherical tensors of weight n . The J -ferroic classification restricted to polar spherical tensors appears as the natural extension of ferroelectricity ($J = 1^-$: spontaneous polarization) and ferroelasticity ($J = 2^+$: electrical quadrupole): The weight J of the transition corresponds to the lowest-weight n pole appearing at the phase transition. Inspection of Table I shows that ferroicity exists up to weight 9, with the exception of weight 8.

B. Spontaneous response function

Each response function is described, in a given reference frame, by a polar Cartesian tensor of rank n and parity $(-1)^n$. Its decomposition into spherical tensors contains polar as well as axial spherical tensors of weight $J \leq n$ and parity $(-1)^n$. The decomposition of usual response-function tensors into irreducible parts is listed in Table II. If some spontaneous spherical tensor appears in this decomposition, some spontaneous Cartesian components of the response function differ from one domain to some others. As shown in Table II, pyroelectricity, piezoelectricity, optical nonlinearities, ..., are fully or partially modified at the 1^- (ferroelectric) transition, while the onset of molecular rotation power⁹ D_0^- is characteristic of 0^- ferroicity. Consequently it is possible to associate with each J^\pm ferroic transition a spontaneous change in a response function, whose orientation differ between domains. This is done in Table III for values of J up to 4.

TABLE II. Decomposition of response-function Cartesian tensors into irreducible spherical tensors. P , E , e , and σ are, respectively, the polarization, electric field, strain, and stress tensors referred to a Cartesian frame.

Response function Cartesian tensor	Constitution relation	Irreducible-spherical- tensor decomposition
Pyroelectricity μ_i	$dP_i = \mu_i dT$	D_1^-
Dielectric constant ϵ_{ij}	$P_i = \epsilon_{ij} E_j$	$D_2^+ + D_0^+$
Piezoelectric tensor Π_{ijk}	$P_i = \Pi_{ijk} \sigma_{jk}$	$2D_1^- + D_2^- + D_3^-$
Second-order dielectric constant ^a $\chi_{ijk}^{(2)}$	$P_i = \chi_{ijk}^{(2)} E_j E_k$	$D_1^- + D_3^-$
Compliance tensor S_{ijkl}	$e_{ij} = S_{ijkl} \sigma_{kl}$	$2D_0^+ + 2D_2^+ + D_4^+$
Electrostriction Photoelasticity $\left. \begin{array}{l} \\ \\ \end{array} \right\} Q_{ijkl}$	$e_{ij} = Q_{ijkl} E_k E_l$ $\Delta \epsilon_{kl} = 2Q_{ijkl} \sigma_{ij}$	$2D_0^+ + D_1^+ + 3D_2^+ + D_3^+ + D_4^+$
Optical activity ^b G_{ijk}	$P_i = G_{ijk} \delta_j E_k$	$D_0^- + D_1^- + D_2^-$
Second-order Electrostriction; Electroelastic effect $\left. \begin{array}{l} \\ \\ \\ \end{array} \right\} A_{ijklm}$	$P_i = A_{ijklm} \sigma_{jk} \sigma_{lm}$ $\Delta S_{jklm} = 2A_{ijklm} E_i$	$4D_1^- + 2D_2^- + 3D_3^- + D_4^- + D_5^-$
Second-order compliance tensor D_{ijklmn}	$e_{ij} = D_{ijklmn} \sigma_{kl} \sigma_{mn}$	$3D_0^+ + D_3^+ + 2D_4^+ + D_6^+$

^aThe Kleinman relations are assumed (i.e., the medium is dispersionless).

^bThe D_1^- component has never been detected.

TABLE III. Response functions and switching forces associated with each spontaneous irreducible spherical tensor.

Spontaneous irreducible spherical tensor	Lowest-rank response-function tensor	Associated switching force	Rank of the response-function tensor	Ferrocity order
0^-	Optical activity (molecular rotatory power)	\dots	3	
1^-	Pyroelectricity	E	1	1
1^+	Electrostriction Photoelasticity	σE^2	4	3
2^-	Piezoelectricity Optical activity (structural)	σE	3	2
2^+	Dielectric constant	σ	2	1
3^-	Piezoelectricity Second-order polarizability	σE	3	2
3^+	Electrostriction Photoelasticity Second-order compliance tensor	σE^2 σ^3	4 6	3 3
4^-	Second-order electrostriction	$\sigma^2 E$	5	3
4^+	Compliance tensor Electrostriction Photoelasticity	σ^2 σE^2	4 4	2 3

C. Switching process

The natural way to switch a domain to another differing in the orientation of a spontaneous extensive quantity of weight J would be to apply the conjugate extensive quantity: an electric field for ferroelectrics, a strain or an electric-field gradient for ferroelastics. However, for transitions of weight greater than 2, this process would be experimentally rather difficult, as one would have to create extremely intense high-order electric field gradients. The other process consists, owing to the difference in orientation of some spontaneous response function, of favoring energetically some domains amidst the other ones by the application of an electric field and/or a stress. This corresponds, in the spherical tensor formalism, to building up a Cartesian tensor by products of symmetrized powers of an electric field and a stress, whose decomposition contains the

spontaneous spherical tensor associated with the spontaneous response function. The lowest possible degree f of such a monomial in electric field (E) and stress (σ) is just the order of ferrocity. The lowest-degree monomials associated with a given D_f^s are listed in Table III, and the switching forces corresponding to any maximum species can be found in Table I. Inspection of the tables shows that the order of ferrocity never exceeds 3. The tertiary ferroics correspond to "switching forces" $\sigma^2 E$, σE^2 , and σ^3 and, generalizing the Newnham and Cross denotations, will be called, respectively, ferroelectrobialastics, ferroelastobielectrics, and ferrotrielastics. Note that ferroelastoelectrics (σE coupling to the piezoelectric tensor) are either 2^- or 3^- ferroics, and that ferrobielectrics (E^2) coincide with ferroelastics (σ), as they form the class of 2^+ ferroics. Any ordinary response function corresponds to an incipient switching process, except the optical-activity tensor which

connects the polarization to the electric field gradient.

It clearly appears that no one-to-one correspondence can be constructed between these three classifications, as no explicit relationship can be found between J (the weight of the ferroic species), n (the rank of the lowest rank Cartesian tensor describing a response function appearing in the ferroic phase), and f (the order of ferroicity). (See Table III.)

V. DESCRIPTION AND PROPERTIES OF FERROIC DOMAIN STRUCTURES

The concept of weight of a ferroic species is not always sufficient to describe completely the domain structure of a ferroic material: Aizu² pointed out the occurrence of simultaneous ferroelectric and ferroelastic domain structure in some materials ($\text{Ba}_2\text{NaNb}_5\text{O}_{15}$, for instance, whose room-temperature ferroic species is $4_2/mmm Fmm2$) where neither the spontaneous polarization orientation alone nor the spontaneous strain orientation alone can specify a given domain. Although the weight of such a species is 1, to assign a given domain one must use the orientation of spontaneous extensive quantities of weight 1 and 2 together. However, one finds that, for $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$, any domain can be specified by the orientation of its spontaneous electric octupole (D_3^-).

Let us consider two different examples: Bismuth titanate ($\text{Bi}_4\text{Te}_3\text{O}_{12}$) belongs at room temperature to the ferroic species $4_2/mmm Fm_x$.¹⁰ Inspection of Table I shows that the spontaneous spherical tensors are $D_1^-, D_1^+, D_2^-, D_2^+, D_3^-, D_3^+$, etc. Thus the weight of the species is 1 (ferroelectric). Let us study the domain structure. With $4_2/mmm$ and m_x possessing, respectively, 16 and 2 different symmetry operations, the material must exhibit 8 different domains. Point group $4_2/mmm$ possesses 10 different IR, 5 of which (excepting the trivial representation) contain the totally symmetric representation of m_x , and are labeled in Koster's notation¹¹ $\Gamma_3^+, \Gamma_3^-, \Gamma_4^-, \Gamma_4^+, \Gamma_5^-$. To each of

these IR (labeled Γ) we associate the largest subgroup \mathcal{G}_Γ of $4_2/mmm$ whose symmetry operations leave invariant the spontaneous components of Γ appearing in the ferroic symmetry, as can be seen on Table IV. Then with each spontaneous tensor D_f^e we associate G_f^e which is the largest subgroup common to all the \mathcal{G}_Γ associated with all the spontaneous Γ appearing in the decomposition of D_f^e on point group $4_2/mmm$. These correspondences are listed in Table IV. The lowest-weight polar spontaneous spherical tensor D_1^- contains Γ_2^- and Γ_5^- . The associated point group G_1^- is the largest subgroup common to $4_2/mmm$ (\mathcal{G}_2^-) and $mm2_y$ (\mathcal{G}_5^-), i.e., m_x , which is the ferroic point group. As G_1^- has been constructed so as to be the largest subgroup of $4_2/mmm$ which leaves invariant the spontaneous quantities transforming like D_1^- , we infer that the spontaneous polarization differs from one domain to any other one: Bismuth titanate is a full ferroelectric. Groups G_f^e up to weight 3 are listed in Table IV: Physical quantities transforming like $D_1^-, D_2^-,$ and D_3^- specify unambiguously a given domain. On the contrary, spontaneous spherical tensors D_1^+, D_2^+, D_3^+ do not differ between any couple of domains forming the average symmetry $2/m$: There are only four different orientations of the ferroelastic spontaneous strain.

The same ideas can be applied to describe the ferroic domain structure of KAlO_2 , which belongs at room temperature to the space symmetry $P2_13$ with pseudosymmetry $Fd3m$.⁸ Although no domain structure has yet been determined, this compound is a candidate to realize the ferroic species $m3mF23$ specified by the spontaneous polar spherical tensors $D_3^-, D_6^+, D_7^-, D_8^-$, the spontaneous axial spherical tensors $D_0^-, D_3^+, D_4^-, \dots$, and the occurrence of four different domains. The weight of this ferroic species is 3. Among the 10 different IR of $m3m$, only Γ_1^-, Γ_2^- , and Γ_2^+ exhibit spontaneous values in the ferroic symmetry 23. Table V shows that the lowest-weight spontaneous polar spherical tensor D_f^e

TABLE IV. Spontaneous spherical tensor analysis of the domain structure of bismuth titanate.

Spontaneous Γ	Group \mathcal{G}_Γ	Spontaneous D_f^e	Associated Γ	Group G_f^e
Γ_3^+	$m_x m_y m_z$	D_1^-	Γ_2^-, Γ_5^-	m_x
Γ_3^+	$2/m_x$	D_1^+	Γ_3^+	$2/m_x$
Γ_2^-	$4mm$	D_2^-	Γ_4^-, Γ_5^-	m_x
Γ_4^-	$\bar{4}_{xy} 2m_x$	D_2^+	Γ_3^+, Γ_5^+	$2/m_x$
Γ_5^-	$mm2_y$	D_3^-	$\Gamma_2^-, \Gamma_4^-, \Gamma_5^-$	m_x
		D_3^+	Γ_3^+, Γ_5^+	$2/m_x$

TABLE V. Spontaneous spherical tensor analysis of the domain structure of potassium aluminate.

Spontaneous Γ	Group \mathcal{G}_Γ	Spontaneous polar D_f^ξ	Associated Γ	Group G_f^ξ	Spontaneous axial D_f^ξ	Associated Γ	Group G_f^ξ
Γ_1^-	432	D_3^-	Γ_2^-	$\bar{4}3m$	D_0^-	Γ_1^-	432
Γ_2^-	$\bar{4}3m$	D_6^+	Γ_2^+	$m3$	D_3^+	Γ_2^+	$m3$
Γ_2^+	$m3$	D_7^-	Γ_2^-	$\bar{4}3m$	D_4^-	Γ_1^-	$\bar{4}3m$
		D_9^-	Γ_1^-, Γ_2^-	23			

whose associated group G_f^ξ coincides with the ferroic group is D_9^- . It describes the lowest-weight spontaneous extensive quantity (a 2^9 pole) whose orientation assigns unambiguously a given domain. $m3mF23$ will be called a $3/9$ ferroic species. Furthermore the four domains labeled from 1 to 4 can be arranged in subsets (called "clusters" by Aizu²) relative to their average symmetry G_f^ξ (see Table VI). Two domains of the same subset exhibit the same D_f^ξ physical properties, albeit two domains belonging to different subsets relative to the same D_f^ξ can be distinguished by the orientation of any D_f^ξ spontaneous response function, and are switchable from one subset to the other by application of the corresponding force. Note that to characterize an eventual domain structure in KAlO_2 , one must perform D_0^- (optical activity), D_3^+ (second-harmonic generation or piezoelectricity), and D_3^+ (photoelasticity) experiments.

The general group-theoretical formalism used to study any ferroic domain structure thus appears straightforward: Let us consider the set $\{\Gamma\}$ of IR of the prototypical point group G_p containing the trivial IR of the ferroic point group G_f . As already pointed out, any spontaneous irreducible spherical tensor contains at least one Γ . To each Γ we associate \mathcal{G}_Γ which is the largest subgroup of G_p whose symmetry

operations leave invariant the spontaneous components of Γ . For each spontaneous D_f^ξ , we define G_f^ξ as the largest subgroup common to all the \mathcal{G}_Γ associated with the Γ contained in D_f^ξ . It is easily shown that G_f^ξ is the largest subgroup of G_p leaving invariant the spontaneous components of D_f^ξ , and that it is a supergroup of G_f .

If the group G_f^ξ associated with the weight of the ferroic species coincides with G_f , the species is fully J -ferroic. Note that any species which can be obtained through an equitranslational phase transition described by a single order parameter¹² is fully ferroic. As a consequence all maximum species are fully ferroic.

Let us show that, if a species is not fully ferroic, one can always find a spontaneous polar spherical tensor of weight lower or equal to 9 whose orientation differs for any couple of domains. As pointed out before, any point group is a subgroup of $m3m$ or $6/mmm$. One establishes that D_6^+ (respectively, D_9^-) splits into the whole set of even (respectively, odd) IR of these two groups. As a consequence, any even (respectively, odd) IR of any prototypic point group is contained in D_6^+ (respectively, D_9^-). If the inversion operation does not belong to G_p , the whole set $\{\Gamma\}$ appears in the decomposition of D_6^+ ; thus G_6^+

TABLE VI. Response functions and switching forces associated with subsets of domains in potassium aluminate.

Intermediate symmetry	Associated subsets of domains	Spontaneous spherical tensors		Associated spontaneous response function	Switching forces
		Polar	Axial		
$\bar{4}3m$	(1,2); (3,4)	$3^-, 7^-, 9^-$		Piezoelectricity	σE
$m3$	(1,3); (2,4)	6^+	3^+	Electrostriction; Photoelasticity	σ^3 or σE^2
432	(1,4); (2,3)	9^-	$0^- 4^-$	Optical-activity Second-order electrostriction	$\sigma^2 E$

TABLE VII. Type of couples of twins in quartz and associated physical properties.

Type	Name	Twinning operations	Curien and Le Corre notation	Coordinate transformation	Change in rotatory power	Change in piezoelectricity
I	Dauphiné	6,2	6'22'	$-x, -y, z$	No	d_{11}
II		$\bar{1}, m'$	$3' \frac{2}{m'}$	$-x, -y, -z$	g_{11}, g_{33}	$d_{11}d_{14}$
III		m, m''	$\bar{6}, 2m'$	x, y, z	$g_{11}g_{33}$	d_{14}

coincides with G_f , and the spontaneous components of D_6^+ differ from one domain to any other one. If G_p contains the inversion operation, two cases must be distinguished: (i) The inversion operation remains in G_f : The spontaneous Γ are all even, and G_6^+ coincides with G_f . (ii) G_f does not contain the inversion operation: It is easily shown that one can always find a path through intermediate groups from G_p to G_f , induced only by odd Γ : It is enough that the first intermediate species leads to the loss of the inversion operation. Thus G_9^- coincides with G_f .

Summing up, we have demonstrated that only two mutually excluding cases can be distinguished: (i) Any domain differs from all the others in the orientation of the lowest-weight spontaneous extensive quantity. These ferroic species are called fully J -ferroic. (ii) If the species is not fully J -ferroic, one can always find spontaneous polar extensive quantities whose orientations differ from one domain to any other one. The lowest-weight multipole fulfilling such a condition corresponds to a weight J' lower or equal to nine. These species will be called J/J' ferroics.

Finally, the domains can be arranged in subsets associated with an averaged symmetry G_f^f : two domains belonging to the same subset exhibit the same D_f^f physical properties.

This concept of averaged symmetry as well as other considerations developed above are very useful for discussing twins. In the case of twins by merohedry, the prototypic phase possesses all the symmetries of the Bravais lattice of the twinned crystal. Any symmetry operation S belonging to G_p and not to G_f transforms one twin into another one. Note that since the prototypic phase and the twinned crystal have the same lattice, the crystallographic axis i ($i = x, y, z$) is invariant with respect to S which can change only its orientation: $S(i) = \mp i$. This fact allowed Curien and Le Corre¹³ to make a very elegant application of the Shoubnikov colored groups to the study of twins. It also determines how optical properties change from one twin to another.

Let us take the example of point group 32 which is

the point group of several well-known crystals; quartz, selenium, tellurium, cinnabar, benzil, ... The prototypic phase has symmetry $6/mmm$ and there are six twinning operations

$$6, \bar{1}, m, 2, m', m''$$

leading to three types of couples of twins, associated with three different intermediate symmetries, as shown in Table VII.

In the case of quartz, Dauphiné twins are well known and correspond to type I. By contrast it is not clear in the literature what exactly is called Brazilian twins. Is it type II or III? As shown by Table VII, notations such as "electrical twins" or "optical twins" are ambiguous since there are changes in piezoelectric properties for the three types while rotatory power changes its sign in type II and III. It is interesting to note that among the three possible averaged symmetries, namely, 622 , $\bar{3}m$, and $\bar{6}m2$, only the first one corresponds to the prototypical symmetry of an effective ferroic transition (weight 3^-), the well-known $\alpha \rightarrow \beta$ quartz transition.

Twins have also been observed in cinnabar. Non-linear optical experiments¹⁴ showed that they are of type III for crystals grown by hydrothermal synthesis.¹⁵ These twins would correspond to a $\bar{6}m2F32$ ferroic species whose associated phase transition has never been detected, while the high-temperature phase of HgS, metacinnabar, has $\bar{4}3m$ symmetry. The observed twin structure of cinnabar is incompatible with a ferroelastic cinnabar-metacinnabar transition which is, in fact, not reversible.

VI. CONCLUSION

The use of the spherical-irreducible-tensor formalism, particularly suitable for the analysis of macroscopic physical quantities has enabled us to build up a natural generalization of the concepts of ferroelectricity and ferroelasticity in terms of J -ferroics associated with the lowest-weight electrical multipole appearing in the ferroic phase. Species up to weight 9 exist,

with the exception of weight 8. Spontaneous spherical tensors permit classification of the response functions differing in orientation between domains, and the domain switching forces. We have shown that the order of ferroicity never exceeds 3, and that, whatever the ferroic species, one can find an extensive quantity of weight lower than or equal to 9 which differs from one domain to another. Thus, the spherical-tensor formalism gives an intrinsic classification of ferroic species and phase transitions, and paves the bridge between the different classifications already proposed by various authors.

*Laboratoire associé au CNRS 250.

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