PHYSICAL REVIEW B VOLUME 16, NUMBER 1 1 JULY 1977

Order-parameter symmetries for the phase transitions of nonmagnetic secondary and higher-order ferroics

Pierre Tolédano
Groupe de Physique Théorique, Faculté des Sciences, 80000-Amiens, France

Jean-Claude Tolédano
Centre National d'Etudes des Télécommunications, 92220-Bagneux, France

(Received 21 January 1977)

A theoretical investigation is presented of the order-parameter symmetries of all possible secondary and higher-order ferroic transitions, (nonmagnetic). These structural phase transitions, which are neither ferroelectric nor ferroelastic, involve the onset of a spontaneous macroscopic quantity represented by a polar tensor of rank higher than 2. The investigation is performed on the basis of the Landau's symmetry criteria for continuous transitions. Particular attention is given to transitions accompanied by a change of the number of atoms in the crystal's unit cell (improper ferroic transitions). Accordingly, the irreducible representations of 147 space groups are examined, corresponding to all the relevant high-symmetry points of their respective Brillouin zones. Eight tables summarize the results by indicating the irreducible representations which are compatible with a secondary or higher-order ferroic transition, and specifying the corresponding space-group change. For each of the predicted transitions, a free-energy expansion is constructed. Twelve different types of expansions are encountered, relative to one-, two-, three-, four-, and six-dimensional order parameters. The form of the term representing the coupling between the order-parameter and the spontaneous macroscopic quantity is also determined. These results are discussed, and compared to the existing experimental data relative to the considered type of transitions, such as those in ammonium chloride, iron sulfide, or quartz. ~~The case~~ of niobium dioxide is treated in detail, and a new interpretation is given for its transition's order parameter.

I. INTRODUCTION

Several currently investigated structural phase transitions,$^{1-3}$ such as the α-β transformation in quartz, do not involve the onset, below the transition's temperature, either of a spontaneous polarization, or of a spontaneous deformation. These transitions are neither ferroelectric[4] nor ferroelastic.[5]

However, they have in common several important features with the two preceding, extensively studied[6] categories of transitions: modification of the point group of the crystal, presence of twinning in the low-symmetry phase,[7] and possible removal of the twins by externally applied forces.[7] This similarity has led Aizu[8] to define the concept of a ferroic crystal which covers ferroelectrics and ferroelastics as well as other types of crystals such as those mentioned above. In an earlier work by Indenbom,[9] a comparable generalization was already implied.

A crystal is said to be ferroic when it can exist in two or more states having equal stabilities in the absence of external forces, and when it has crystal structures which only differ in their spatial orientations. When simultaneously present in a given crystal, these differently oriented structures constitute ferroic domains. Each state can be considered as slightly modified with respect to a "prototypic" structure of higher symmetry, invariant by the set of symmetry operations of all the differently oriented states. The definition of a ferroic also specifies the possibility of reversibly switching the crystal from one orientation state to another by application of external forces. However, the latter condition can be ignored when ferroics are considered from a crystallographic point of view.[10]

Ferroelectrics and ferroelastics clearly comply with the former definition. In these two types of crystals, the different orientation states are characterized at macroscopic level by the direction of a spontaneous polarization or by the orientation of a spontaneous strain tensor. In a similar way, the orientation states of all ferroics can be characterized by tensorial quantities which take different values in the different states when referred to a common system of axes. One can distinguish various types of ferroics on the basis of the rank of the lowest-rank polar tensor[11] characterizing the different orientation states of the crystal. Thus, polar tensors of rank one (polarization), two (strain), three (piezoelectric modulus), and four (elastic modulus), are, respectively, associated with ferroelectrics, ferroelastics, and the new types of ferroics labelled ferroelastoelectrics and ferrobielastics.[12] More complex ferroics are also conceivable[12] for which the relevant polar tensor is of rank higher than four. On the other hand, axial tensors can be considered, leading to the definition of magnetic ferroic species. For instance, ferromagnetics are those ferroics which are characterized by an axial vector.

A classification of ferroics has been based[8,12] on the form of the difference of free-energy ΔF between two orientation states, expressed as a power series of the electric field E_i, the mechanical stress σ_{ij}, and the magnetic field H_i. A primary ferroic is defined as one for which the lowest-power term in the ΔF expansion is linear in E_i, σ_{ij}, or H_i. Primary ferroics are composed of ferroelectrics, ferroelastics, and ferromagnetics. When the lowest-power term in ΔF is a bilinear function of the above forces, we have to deal with a secondary ferroic. Finally higher-order ferroics include all ferroics for which the lowest-power term in ΔF is of degree higher than two.

As seen from a symmetry point of view,[13] it is possible to identify nonmagnetic secondary ferroics as those characterized by polar tensors of rank three or four. Likewise, nonmagnetic higher-order ferroics correspond to polar tensors of rank higher than four.

Although the preceding considerations do not imply that a ferroic crystal undergoes a phase transition, it is clear that, similarly to ferroelectrics and ferroelastics, most ferroics will transform at a certain "Curie" temperature into a phase possessing the symmetry of the prototypic structure. This phase transition can be studied by using the Landau's theory of phase transitions[14] and, in particular, an order parameter can be defined for it. In the case of ferroelectrics and of ferroelastics, and a number of studies[15-17] have used the Landau's theory in order to account for the symmetry change observed at the Curie point. They have also shown that the behavior of the macroscopic quantities (such as the polarization or the dielectric susceptibility) on varying the temperature closely depends on the symmetry properties of the transition's order parameter.[15-17]

No systematic investigation has been performed up to now of the order-parameter symmetries and possible symmetry changes relative to secondary and higher-order ferroic transitions (SHFT). An additional stimulation to such a work can be drawn from the recent results[18] obtained on niobium dioxide, a material which can be classified as a secondary ferroic[12] (ferrobielastic). It was pointed out by Mukamel[18] that a new situation occurred for the transition of NbO_2 with respect to the renormalization-group theory of critical exponents,[19] owing to the unusual four-dimensionality of its order parameter and to the particular tetragonal anisotropy of the expansion[20] associated with its transition.

In this paper we present an exhaustive study of the order-parameter symmetries and space-group changes for all possible SHFT. This theoretical analysis has been performed on the basis of Landau's symmetry criteria for continuous (second-order) transitions.[14] It is restricted to nonmagnetic ferroics. Accordingly we have examined the irreducible representations of 147 crystallographic space groups which are likely to constitute the invariance group of the prototypic phase. Consideration of the space-group representations instead of the simpler point-group ones is known to be necessary if one wants to account for the transitions which are accompanied by a modification of the crystal's primitive translations.

The paper is divided into three sections. In Sec. II we briefly review the method used to apply the Landau's theory to the SHFT. Extensive use is made of results obtained in a similar work[17] in which we analyzed the order parameters of ferroelectric nonferroelastic transitions. In Sec. III the results are summarized in table form for the different types of ferroics and for the different crystalline systems. For all the predicted transitions, free-energy expansions are constructed. Finally, the available experimental data are compared to the theoretical results. Particular attention is given to the controversial case of niobium dioxide.

II. THEORETICAL PROCEDURE

A secondary or higher-order ferroic species is crystallographically defined by the point symmetries of the ferroic and prototypic phases.[21] This set of point groups determines entirely the rank and particular components of the tensorial quantities which distinguish the different orientation states of the ferroic crystal. Newnham and Cross[12] have worked out the 34 secondary or higher-order ferroic species which can be decomposed into 15 ferroelastoelectric, 5 ferrobielastic, 10 simultaneously ferroelastoelectric and ferrobielastic, and 4 higher-order ferroic species. We have reproduced them in Table I together with the corresponding tensorial components characterizing the ferroic states. The prototypic phase belongs to one of 17 crystal classes of the orthorhombic, tetragonal, trigonal, hexagonal, and cubic systems. We note that the two point groups defining each species belong to the same crystalline system, providing that the hexagonal and trigonal systems are considered as a single system.

TABLE I. Secondary- and higher-order ferroic species. The set of point groups defining each species is indicated, as well as the tensorial components characterizing the different ferroic domains. d_{ij} are components of the piezoelectricity tensor in the Voigt contracted notation of the indices (Ref. 11). Likewise C_{ij} are components of the elastic stiffness tensor. L_{ijk} is a polar tensor of rank six (third-order elastic constants). All tensors are referred to the standard setting of axes (Ref. 11). For most species the change in the number of symmetry operations is twofold, and there are two domain orientations characterized by opposite values of the tensorial components. Some species involve a fourfold decrease of point symmetry and four types of domains. For these species four sets of tensorial components distinguish the domains. We have only indicated the set for one domain orientation.

Type of ferroic	Ferroic species		Spontaneous tensorial components
Ferroelastoelectric	mmm	222	$(d_{14};\ d_{25};\ d_{36})$
	$4/m$	$\bar{4}$	$(d_{14};\ d_{15};\ d_{31};\ d_{36})$
	$4/mmm$	422	d_{14}
	$4/mmm$	$\bar{4}2m$	$(d_{14};\ d_{36})$
	$\bar{3}m$	32	$(d_{14};\ d_{11})$
	$6/m$	$\bar{6}$	$(d_{11};\ d_{22})$
	$\bar{6}m2$	$\bar{6}$	d_{11}
	$6mm$	6	d_{14}
	$6/mmm$	$\bar{6}$	$d_{11};\ d_{22}$
	$6/mmm$	$\bar{6}m2$	d_{22}
	$6/mmm$	622	d_{14}
	$m3$	23	d_{14}
	432	23	d_{14}
	$m3m$	$\bar{4}3m$	d_{14}
	$m3m$	23	$d_{14};\begin{cases}L_{113}-L_{112}\\L_{166}-L_{155}\end{cases}$
Ferrobielastic	$4/mmm$	$4/m$	C_{16}
	$\bar{3}m$	$\bar{3}$	C_{15}
	$6/m$	$\bar{3}$	$(C_{14};\ C_{25})$
	$6/mmm$	$\bar{3}m$	C_{14}
	$6/mmm$	$\bar{3}$	$C_{14};\ C_{25}$
Ferroelastoelectric and ferrobielastic	$\bar{4}2m$	$\bar{4}$	$(d_{15};\ d_{31};\ C_{16})$
	$4mm$	4	$(d_{14};\ C_{16})$
	$4/mmm$	$\bar{4}$	$d_{14};\ d_{15};\ d_{31};\ d_{36};\ C_{16}$
	$3m$	3	$(d_{11};\ d_{14};\ C_{15})$
	6	3	$(d_{11};\ d_{22};\ C_{14};\ C_{25})$
	$\bar{6}m2$	32	$(d_{14};\ C_{14})$
	622	32	$(d_{11};\ C_{14})$
	$6mm$	$3m$	$(d_{11};\ C_{14})$
	$6mm$	3	$d_{11};\ d_{22};\ d_{14};\ C_{14};\ C_{25}$
	$6/mmm$	32	$d_{11};\ d_{14};\ C_{14}$
Higher-order ferroics	$6/mmm$	$6/m$	$(L_{116};\ L_{145})$
	$\bar{4}3m$	23	$(L_{113}-L_{112};\ L_{166}-L_{155})$
	$m3m$	$m3$	$(L_{113}-L_{112};\ L_{166}-L_{155})$
	$m3m$	432	Ninth-rank polar tensor

A. Application of Landau's theory to the SHFT

Landau's theory of continuous phase transitions[14] shows that the order parameter (OP) of a transition transforms according to a physically irreducible representation (IR) of the space-group G_0 of the high-symmetry phase of the crystal. A physically IR is either a real IR of G_0 or the direct sum of two complex-conjugate IR of G_0. In order to determine the OP symmetries of all possible SHFT taking place between a ferroic phase and its prototype, it is therefore necessary to examine the IR of all the space groups associated to the 17 crystal classes mentioned above. There are 147 such space groups.

Each IR of a given space group can be denoted $\Gamma_n(k^*)$ and identified by two quantities.[22] The star k^*, represented by a $\vec{k}$ vector of the first Brillouin zone (BZ), specifies the translational symmetry properties of the basis functions of $\Gamma_n(k^*)$. The n index specifies the small IR, denoted τ_n, of the little group[22] $G(\vec{k})$. The dimension of $\Gamma_n(k^*)$ is the product of the dimension of τ_n and of the number of arms in the star k^*. This dimension is equal to the number of components of the OP. A given space group has an infinite number of IR, as an infinity of $\vec{k}$ vectors corresponding to distinct stars can be found in the BZ. However, the number of these IR which have actually to be considered in the study of an SHFT is reduced by several restrictive rules.

In the first place, if we limit the scope of the present work to continuous (second-order) transitions between strictly periodic crystalline structures, the general theory of Landau and Lifschitz[14] imposes two conditions to an acceptable IR:

(a) The antisymmetrized square, noted $\{\Gamma\}^2$ of $\Gamma_n(k^*)$ must not have any IR in common with the vector representation of G_0.

(b) The symmetrized third power of $\Gamma_n(k^*)$, noted $[\Gamma]^3$, must not contain the totally symmetric IR of G_0.

The physical meaning of these criteria, as well as the detailed procedure of their application have been recalled recently by the present authors in the work mentioned above,[17] referred to hereafter as TT.

First, the $\{\Gamma\}^2$ criterion selects a few acceptable stars in each BZ which correspond to the BZ center and to definite high-symmetry[23] points of the BZ surface. The latter points were listed in TT for all the crystalline systems but the cubic one. Table II completes the list and contains the acceptable points of the cubic Brillouin zones. In addition, for each acceptable BZ point, and for each space group, some of the IR are not compatible with the $\{\Gamma\}^2$ criterion. They can be found by using the space-group character tables,[24] according to a procedure indicated in TT.[17]

The $[\Gamma]^3$ criterion is necessarily obeyed by all the IR whose stars verify the relation

$$\vec{k}_i + \vec{k}_j + \vec{k}_1 \neq 0 \tag{1}$$

for any $(\vec{k}_i, \vec{k}_j, \vec{k}_1)$ belonging to the considered star k^*.

When the preceding rule is not verified an IR can nevertheless satisfy the $[\Gamma]^3$ criterion. However, in this case, one has to work out the matrices of the considered IR in order to determine the symmetry properties of the basis functions of $\Gamma_n(k^*)$. One is then able to check directly condition (b) by finding out if an invariant exists in the $[\Gamma]^3$ space.[22]

Several additional restrictions have to be considered in the study of an SHFT. As emphasized by Birman,[25] a given IR of the space group G_0 is compatible with a transition between G_0 and one of its subgroups G, if the restriction to G of $\Gamma_n(k^*)$ contains the totally symmetric IR of G. When dealing with a SHFT any subgroup G of G_0

TABLE II. Modifications of Bravais lattice occuring in the cubic system and related to high-symmetry points of the BZ. The considered points correspond to a $\vec{k}$ vector whose invariance point group possesses a central point (Ref. 14 and 17). The labelling of the points is the one used by Zak (Ref. 24). Column (a): coordinate of the $\vec{k}$ vector defining each point and referring to the primitive translations of the reciprocal lattice. The Bravais lattices of the two phases belong to the same crystalline system.

High symmetry Bravais lattice	Brillouin-zone point	(a)	Number of arms in the star	Ferroic Bravais lattice	Unit-cell expansion
P	Γ	$0\ 0\ 0$	1	P	1
	R	$\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$	1	F	2
	X	$0\ \frac{1}{2}\ 0$	3	P	8
	M	$\frac{1}{2}\ \frac{1}{2}\ 0$	3	I	4
I	Γ	$0\ 0\ 0$	1	I	1
	H	$\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$	1	P	2
	N	$\frac{1}{2}\ 0\ 0$	6	I	8
	P [a]	$\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4}$	2	F	4
F	Γ	$0\ 0\ 0$	1	F	1
	X	$\frac{1}{2}\ \frac{1}{2}\ 0$	3	P	4
	W [a]	$\frac{3}{4}\ \frac{1}{2}\ \frac{1}{4}$	6	P	32
	L	$\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$	4	F	8

[a] Brillouin-zone points whose $\vec{k}$ vector is not equivalent to $-\vec{k}$.

is not acceptable. The following conditions must be respected:

(c) The change in point symmetry between G_0 and G has to coincide with one of the species of Table I.

(d) As shown in TT, when a transition preserves the crystalline system, the Bravais lattice of G is unambiguously related to that of G_0 and to the star of the considered IR. More precisely, the translation group of G is composed of all the translations $\vec{T}$ which verify the set of equations

$$e^{i\vec{k}_j\cdot\vec{T}}=1\,, \tag{2}$$

where $\vec{k}_j$ is any vector in the star k^*, and $\vec{T}$ belongs to G_0. These equations correspond to the maximum loss of translational symmetry compatible with the star k^*. Thus each BZ point is associated with a change of the Bravais lattice indicated in Table II for the cubic system and indicated previously in TT for the other systems.

(e) The nonprimitive translation $\vec{t}$ associated with each point operation of G has to be equal either to the corresponding nonprimitive translation $\vec{t}_0$ of G_0 or to the sum of $\vec{t}_0$ and a primitive translation of G_0 not belonging to G, i.e., not fulfilling Eqs. (2).

In summary, the procedure to determine if an SHFT is induced by a given IR of G_0 is to select the subgroups of G_0 whose point group, Bravais lattice, and nonprimitive translations are specified by conditions (c)–(e), and to check with the help of the space-group character tables[24] the compatibility of these subgroups with Birman's condition.

Two rules demonstrated in TT are useful to systematically discard many IR:

(f) When $\Gamma_n(k^*)$ is a real and one-dimensional IR, with $\vec{k}\neq 0$, it induces no change in the point symmetry of the crystal.

(g) Let $\Gamma_n(k^*)$ be in IR whose star k^* has two arms with each $\vec{k}$ equivalent to $-\vec{k}$. If the small IR (τ_n) is real and one-dimensional, no point-symmetry change occurring within the crystalline system of G_0 is compatible with $\Gamma_n(k^*)$.

We note that the procedure outlined above sets necessary conditions for the occurrence of an SHFT and allows us to work out the corresponding space-group change. It does not warrant that the determined ferroic phase constitutes the actual equilibrium state of the crystal. In agreement with the Landau's theory,[14] one must check that this phase corresponds to the absolute minimum of the transition's free-energy expansion.[14] However the former procedure restricts the necessity of constructing a free-energy expansion to only those cases where the former necessary conditions are verified.

B. Proper and improper ferroic transitions

The free-energy expansion F is a function of the quantities varying rapidly in the vicinity of the transition, i.e., the order parameter and the relevant macroscopical quantities which can couple to it. F is an invariant function under the symmetry operations of the space group G_0.[14,22]

At an SHFT, the lowering of point symmetry determines the onset of nonzero "spontaneous" values for certain tensorial components which vanish by symmetry in the prototypic phase. These macroscopical quantities are identical to the ones characterizing the different orientation states of the ferroic phase, and are therefore those indicated by Table I for the various species. They must be included in the free-energy expansion, as their variation is significant near the transition. Consequently the expansion F will contain three kinds of invariant terms.

The first ones are invariants of even powers of the OP components. In general, for discussing the symmetry change, one can limit the expansion to the fourth power. The second ones are invariants of the relevant tensorial components. Quadratic terms are sufficient to derive the behavior of these components.[15,17] The third kind of term is composed of "mixed" invariants of the OP and of the tensorial components; they represent the coupling between the OP and the tensorial components. All the preceding invariant terms can be constructed by standard projector techniques,[22] using the matrices of the IR associated with the transition.[26]

Similar to the case of ferroelectric and ferroelastic phase transitions, one can distinguish two types of SHFT on the basis of their OP symmetries.[15,16]

A "proper" SHFT will be characterized by an OP transforming according to the same IR of G_0 as the tensorial components relative to the considered ferroic species. Such an IR necessarily corresponds to the center of the BZ of G_0 (Γ point). It induces no modification of the translational symmetry of the crystal. As an SHFT preserves the crystalline system, the Bravais lattices of both phases are the same. The free energy F of a proper SHFT could, in principle, be expanded exclusively as a function of the tensorial quantities taken as the OP of the transition. In Sec. III we have preferred to use an OP, physically unidentified, coupled linearly to the various tensorial components possessing the same symmetry properties.

An "improper" SHFT has an OP transforming according to an IR of G_0 which is distinct from that of the spontaneous tensorial components. The onset of nonzero values for the latter quantities is a secondary effect of the transition, arising from the nonlinear coupling of these macroscopic components to the OP. In particular, all the SHFT whose OP is associated with a nonzero $\vec{k}$ vector of the BZ of G_0 are expected to be improper. Levanyuk *et al.*[15] have shown in the case of improper ferroelectrics that the mixed invariant in F must depend linearly on the polarization. Otherwise no spontaneous value of this quantity can arise at the transition. Likewise, at an SHFT, the mixed invariant has to be linear in the relevant tensorial quantities. Consequently, the power of the OP in this term has to be greater than one since the coupling is nonlinear.

The power of the OP contribution to the mixed invariant has been defined as the faintness index of the transition with respect to its ferroic properties.[16] Thus a proper ferroic has a faintness index equal to one, while an improper ferroic is characterized by a faintness index greater than one. The value of the faintness index determines the qualitative behavior of the various macroscopical quantities near the transition. For instance, at a ferroelastoelectric transition having a faintness index of four, the spontaneous piezoelectric components will vary as the fourth power of the OP.

III. RESULTS AND DISCUSSION

In this section we describe the results relative to the order-parameter symmetries and space-group changes for proper and improper SHFT and compare them to the experimental data.

The OP symmetries for proper SHFT have also been examined in a recent work by Janovec *et al.*[27] who studied the symmetry changes induced by the point-group representations. The OP of the proper SHFT are all one dimensional and they correspond to a lowering of point symmetry of the crystal by a factor of 2.[14] Hence several of the ferroic species listed in Table I, which involve a greater decrease of point symmetry, cannot occur during a proper SHFT (for instance, $m3m \rightarrow 23$, or $4/mmm \rightarrow \bar{4}$).

The results relative to the OP symmetries of continuous SHFT are summarized in Tables III–X. For the sake of completeness we have included in the tables the proper transitions previously treated by Janovec *et al.*[27] For these transitions we have worked out, effectively, the equitranslational subgroups of each of the considered space groups; the former authors only indicated the change in point symmetry.

A. Organization and use of the tables

Tables III–VI are devoted to ferroelastoelectric (FEE) phase transitions, Table VII to ferrobielastics (FB), Tables VIII and IX to transitions which are simultaneously FEE and FB, and Table X to higher-order ferroic transitions (HOF). In each category the tables are ordered according to the crystalline system common to both phases of the crystal and to the space group of the high-symmetry phase.

First, for each space group the IR which are compatible with the $\{\Gamma\}^2$ criterion are specified. As pointed out in TT, this criterion is necessarily

TABLE III. Ferroelastoelectric transitions in the orthorhombic system. A single transition is possible at a BZ boundary point and is not shown in the table: $Fddd \rightarrow F222$ (τ_2) at the R point (orthorhombic F lattice). It involves an eightfold expansion of the unit cell, and corresponds to the (f_1) type of free-energy expansion (see Table XI). All other transitions occur at the BZ center and are indicated in this table. The two phases are equitranslational.

High-symmetry space group	Low-symmetry space group	High-symmetry space group	Low-symmetry space group
$Pmmm$	$P222$	$Pbca$	$P2_12_12_1$
$Pnnn$	$P222$	$Pnma$	$P2_12_12_1$
$Pccm$	$P222$	$Cmmm$	$C222$
$Pban$	$P222$	$Cmcm$	$C222_1$
$Pmma$	$P2_12_12$	$Cmca$	$C222_1$
$Pnna$	$P22_12$	$Cccm$	$C222$
$Pmna$	$P222_1$	$Cmma$	$C222$
$Pcca$	$P2_122$	$Ccca$	$C222$
$Pbam$	$P2_12_12$	$Fmmm$	$F222$
$Pccn$	$P2_12_12$	$Fddd$	$F222$
$Pbcm$	$P22_12_1$	$Immm$	$I222$
$Pnnm$	$P2_12_12$	$Ibam$	$I222$
$Pmmn$	$P2_12_12$	$Ibca$	$I2_12_12_1$
$Pbcn$	$P2_122_1$	$Imma$	$I2_12_12_1$

TABLE IV. Ferroelastoelectric transitions in the tetragonal system. The labelling of the high-symmetry points of the BZ and of the small representations τ_n refer to the tables of Zak *et al.* (Ref. 24). Column $\{\Gamma\}^2$: the IR which fulfill the $\{\Gamma\}^2$ criterion are specified by their small representation τ_n. "all" means that all multidimensional physically IR fulfill the $\{\Gamma\}^2$ criterion, while a dot means that none satisfy this criterion. Each possible FEE transition is indicated by the space group of the FEE phase followed by the symbol of the representation which induces the transition. At the Γ point τ_n is only indicated for the first space group of each class. Column (a): order-parameter dimension. Column (b): type of free-energy expansion: (refer to Table XI).

High-symmetry space-group	BZ point	$\{\Gamma\}^2$	Ferroelastoelectric space-group	(a)	(b)
$P4/m$	Γ	all	$P\bar{4}(\tau_6)$	1	a
	M		•		
	Z		•		
	A		•		
	R		•		
	X		•		
$P4_2/m$	Γ	all	$P\bar{4}$	1	a
	M		•		
	Z	τ_2	•		
	A		•		
	R	all	•		
	X		•		
$P4/n$	Γ		$P\bar{4}$	1	a
	M	τ_2	•		
	Z	all	•		
	A	τ_2	•		
	R	•			
	X				
$P4_2/n$	Γ		$P\bar{4}$	1	a
	M	τ_2	•		
	Z		•		
	A	all	•		
	R				
	X				
$I4/m$	Γ		$I\bar{4}$	1	a
	Z	all	•		
	X		•		
	N		•		
	A	τ_1, τ_2	•		
$I4_1/a$	Γ		$I\bar{4}$	1	a
	Z	τ_2	•		
	X	•			
	N	all	$I\bar{4}(\tau_1, \tau_2)$	4	f_2
	A	•			
$P4/mmm$	Γ	all	$P\bar{4}2m(\tau_8)$; $P\bar{4}m2(\tau_9)$ $P422(\tau_6)$	1	a
	M		•		
	Z		•		
	A		•		
	R		•		
	X				
$P4/mcc$	Γ		$P422$; $P\bar{4}2c$; $P\bar{4}c2$	1	a
	M	•			
	Z	τ_1, τ_2	$P422(\tau_1)P4_222(\tau_2)$	2	b
	A		$I422(\tau_1, \tau_2)$	2	b
	R	•			
	X	all	•		
$P4/nbm$	Γ		$P422$; $P\bar{4}2m$; $P\bar{4}b2$	1	a
	M	τ_1, τ_2	$P422(\tau_1)$, $P42_12(\tau_2)$	2	b
	Z	all	•		
	A	τ_1, τ_2	$I422(\tau_1, \tau_2)$	2	b
	R	•			
	X				
$P4/nnc$	Γ		$P422$, $P\bar{4}2c$, $P\bar{4}n2$	1	a
	M	τ_3, τ_4	$P422(\tau_3)$, $P42_12(\tau_4)$	2	b
	Z	•			
	A	τ_3, τ_4	$I422(\tau_3, \tau_4)$	2	b
	R	•			
	X				
$P4/mbm$	Γ	all	$P42_12$, $P\bar{4}2_1m$, $P\bar{4}b2$	1	a
	M		•		
	Z				
	A		•		
	R	•			
	X				
$P4/mnc$	Γ		$P4_22_12$, $P\bar{4}2_1c$, $P\bar{4}n2$	1	a
	M	all	•		
	Z	•			
	A	τ_1, τ_2	$I\bar{4}2d(\tau_1, \tau_2)$	2	b
	R	all	•		
	X	•			
$P4/nmm$	Γ	all	$P422$;$P\bar{4}2_1m$;$P\bar{4}m2$	1	a
	M		$P\bar{4}2m(\tau_3)$;$P\bar{4}2_1m(\tau_4)$	2	b
	Z		•		
	A		$I\bar{4}2m(\tau_3, \tau_4)$	2	b
	R	•			
	X				
$P4/ncc$	Γ		$P42_12$; $P\bar{4}2c$, $P\bar{4}c2$	1	a
	M	all	$P\bar{4}2c(\tau_2)$, $P\bar{4}2_1c(\tau_1)$	2	b
	Z	•			
	A				
	R				
	X				
$P4_2/mmc$	Γ		$P4_222$, $P\bar{4}2c$, $P\bar{4}m2$	1	a
	M	all	•		
	Z	τ_3, τ_4	$[P4_122, P4_322](\tau_3, \tau_4)$	2	b
	A		$I4_122(\tau_3, \tau_4)$	2	b
	R	all	•		
	X		•		
$P4_2/mcm$	Γ	all	$P4_222$, $P\bar{4}2m$, $P\bar{4}c2$	1	a
	M		•		
	Z	τ_3, τ_4	$[P4_122, P4_322](\tau_3, \tau_4)$	2	b
	A		$I4_122(\tau_3, \tau_4)$	2	b
	R	•			
	X	all	•		
$P4_2/nbc$	Γ		$P4_222$, $P\bar{4}2c$, $P\bar{4}b2$	1	a
	M	τ_3, τ_4	$P4_222(\tau_3)$, $P4_22_12(\tau_4)$	2	b
	Z		$[P4_122, P4_322](\tau_3, \tau_4)$	2	b
	A	•			
	R				
	X				
$P4_2/nnm$	Γ		$P4_22_12$, $P\bar{4}2m$, $P\bar{4}n2$	1	a
	M	τ_3, τ_4	$P4_222(\tau_3)$, $P4_22_12(\tau_4)$	2	b
	Z		$[P4_122, P4_322](\tau_3, \tau_4)$	2	b
	A	all	•		
	R	•			
	X				
$P4_2/mbc$	Γ		$P4_22_12$, $P\bar{4}2_1c$, $P\bar{4}b2$	1	a
	M	all	•		
	Z	τ_3, τ_4	$[P4_122, P4_322](\tau_3, \tau_4)$	2	b
	A	•			
	R				
	X				
$P4_2/mnm$	Γ		$P4_22_12$, $P\bar{4}2_1m$, $P\bar{4}n2$	1	a
	M	all	•		
	Z	τ_3, τ_4	$[P4_12_12, P4_32_12](\tau_3, \tau_4)$	2	b
	A	all	$I\bar{4}2d(\tau_1, \tau_2)$	2	b
	R		•		
	X	•			
$P4_2/nmc$	Γ		$P4_22_12$, $P\bar{4}2_1c$, $P\bar{4}m2$	1	a
	M	all	$P\bar{4}2m(\tau_4)$, $P\bar{4}2_1m(\tau_3)$	2	b
	Z	τ_3, τ_4	$[P4_122, P4_322](\tau_3, \tau_4)$	2	b
	A	τ_1, τ_2	$I\bar{4}2m(\tau_1, \tau_2)$	2	b
	R	•			
	X				
$P4_2/ncm$	Γ		$P4_22_12$, $P\bar{4}2_1m$, $P\bar{4}c2$	1	a
	M	all	$P\bar{4}2c(\tau_3)$, $P\bar{4}2_1c(\tau_4)$	2	b
	Z	τ_3, τ_4	$[P4_12_12, P4_32_12](\tau_3, \tau_4)$	2	b
	A	all	•		
	R	•			
	X				
$I4/mmm$	Γ		$I422$, $I\bar{4}2m$, $I\bar{4}m2$	1	a
	Z	all	•		
	X		•		
	N		•		
	A	τ_1, τ_2 τ_3, τ_4	•		
$I4/mcm$	Γ		$I422$, $I\bar{4}2m$, $I\bar{4}c2$	1	a
	Z	all	•		
	X		•		
	N	•			
	A				
$I4_1/amd$	Γ		$I4_122$, $I\bar{4}2d$, $I\bar{4}m2$	1	a
	Z	τ_3, τ_4	$[P4_122, P4_322](\tau_3, \tau_4)$	2	b
	X	•			
	N	all	$I\bar{4}m2(\tau_1, \tau_4)I\bar{4}c2(\tau_2, \tau_3)$	4	f_2
	A	•			
$I4_1/acd$	Γ		$I4_122$, $I\bar{4}2d$, $I\bar{4}c2$	1	a
	Z	τ_3, τ_4	$[P4_12_12, P4_32_12](\tau_3, \tau_4)$	2	b
	X	•			
	N				
	A				

TABLE V. Ferroelastoelectric transitions in the trigonal-hexagonal system. All columns have the same content as in Table IV. For the Γ, M, and K points, τ_n is indicated for the first space group of each class.

High-symmetry space-group	BZ point	$\{\Gamma\}^2$	Ferroelastoelectric space-group	(a)	(b)
$P\bar{3}1m$	Γ	all	$P312(\tau_5)$	1	a
	A		●		
	M		$P312(\tau_3)$	3	e
	L		●		
	H	●			
	K				
$P\bar{3}1c$	Γ		$P312$	1	a
	A	●			
	M	all	$P312$	3	e
	L	●			
	H				
	K				
$P\bar{3}m1$	Γ	all	$P321$	1	a
	A		●		
	M		$P321$	3	e
	L		●		
	H	●			
	K				
$P\bar{3}c1$	Γ		$P321$	1	a
	A	●			
	M	all	$P321$	3	e
	L	●			
	H				
	K				
$R\bar{3}m$	Γ	all	$R32$	1	a
	A		●		
	M		$R32$	3	e
	L		●		
	H	●			
	K				
$R\bar{3}c$	Γ		$R32$	1	a
	Z	●			
	X	all	$R32$	3	e
	A	●			
$P6/m$	Γ	all	$P\bar{6}(\tau_2)$	1	a
	A		●		
	M		$P\bar{6}(\tau_4)$	3	e
	L		●		
	H	τ_1, τ_4	●		
	K		●		
$P6_3/m$	Γ		$P\bar{6}$	1	a
	A	●			
	M	all	$P\bar{6}$	3	e
	L	●			
	H				
	K	τ_1, τ_4	●		
$P6mm$	Γ	all	$P6(\tau_2)$	1	a
	A		●		
	M		$P6(\tau_3)$	3	e
	L		●		
	H	τ_1, τ_2	●		
	K		$P6(\tau_2)$	2	d
$P6cc$	Γ		$P6$	1	a
	A	●			
	M	all	$P6$	3	e
	L	●			
	H	●			
	K	τ_1, τ_2	$P6$	2	d
$P6_3cm$	Γ		$P6_3$	1	a
	A	●			
	M	all	$P6_3$	3	e
	L	●			
	H	●			
	K	τ_1, τ_2	$P6_3$	2	d
$P6_3mc$	Γ		$P6_3$	1	a
	A	●			
	M	all	$P6_3$	3	e
	L	●			
	H	τ_3	●		
	K	τ_1, τ_2	$P6_3$	2	d
$P\bar{6}m2$	Γ	all	$P\bar{6}(\tau_2)$	1	a
	A		●		
	M		$P\bar{6}(\tau_2)$	3	e
	L		●		
	H	τ_1, τ_4	●		
	K		●		
$P\bar{6}c2$	Γ		$P\bar{6}$	1	a
	A	●			
	M	all	$P\bar{6}$	3	e
	L	●			
	H	●			
	K	τ_1, τ_4	●		
$P\bar{6}2m$	Γ	all	$P\bar{6}(\tau_2)$	1	a
	A		●		
	M		$P\bar{6}$	3	e
	L		●		
	H	τ_1, τ_2 τ_4, τ_5	●		
	K		$P\bar{6}(\tau_2)$	2	d
$P\bar{6}2c$	Γ		$P\bar{6}$	1	a
	A	●			
	M	all	$P\bar{6}$	3	e
	L	●			
	H	$\tau_2 + \tau_3$	●		
	K	τ_1, τ_2 τ_4, τ_5	$P\bar{6}(\tau_2)$	2	d
$P6/mmm$	Γ	all	$(P622(\tau_7), P\bar{6}m2(\tau_{10}),$ $P\bar{6}2m(\tau_9)$	1	a
	A		●		
	M		$(P622(\tau_5), P\bar{6}m2(\tau_7),$ $P\bar{6}2m(\tau_6)$	3	e
	L		●		
	H	τ_1, τ_2 τ_4, τ_5	●		
	K		$P622(\tau_4), P\bar{6}2m(\tau_2)$	2	d
$P6/mcc$	Γ		$P622, P\bar{6}c2, P\bar{6}2c$	1	a
	A	●			
	M	all	$P622, P\bar{6}c2, P\bar{6}2c$	3	e
	L	●			
	H	●			
	K	τ_1, τ_2 τ_4, τ_5	$P622, P\bar{6}2c$	2	d
$P6_3/mcm$	Γ		$P6_322, P\bar{6}c2, P\bar{6}2m$	1	a
	A	●			
	M	all	$P6_322, P\bar{6}c2, P\bar{6}2m$	3	e
	L	●			
	H	●			
	K	τ_1, τ_2 τ_4, τ_5	$P6_322, P\bar{6}2c$	2	d
$P6_3/mmc$	Γ		$P6_322, P\bar{6}m2, P\bar{6}2c$	1	a
	A	●			
	M	all	$P6_322, P\bar{6}m2, P\bar{6}2c$	3	e
	L	●			
	H	●			
	K	τ_1, τ_2 τ_4, τ_5	$P6_322, P\bar{6}2m$	2	d

fulfilled by real one-dimensional IR. Thus, the tables only indicate the results for multidimensional IR which are identified by the corresponding BZ point and by their small representation τ_n, whose labelling refers to the space-group character tables of Zak *et al.*[24] Some of the crystal classes (for instance, $4/mmm$ or $m3m$) appear in several tables. The results relative to the $\{\Gamma\}^2$ criterion have been reproduced only in the first table where they occur.

As stated in Sec. II, transitions induced by an IR not fulfilling the $\{\Gamma\}^2$ symmetry criterion are outside the scope of the present work. Consequently, the compatibility of a given IR with an SHFT has only been investigated for those IR which fulfill this criterion.

When an SHFT is compatible with $\Gamma_n(k^*)$, the space group of the ferroic phase is specified together with the small-representation τ_n relative to $\Gamma_n(k^*)$. It can happen that an identical space-group change is determined by several IR corresponding to the same BZ point. In that case, the symbols for the small representations are grouped together between brackets following the ferroic space group. It can also happen that SHFT towards different space groups are induced by the same IR. This situation is indicated by grouping the symbols of the various ferroic space groups between brackets. When $\Gamma_n(k^*)$ is associated with another type of symmetry change (ferroelectric, ferroelastic, or equi-orientational), no space group has been indicated for the low-symmetry phase.

In addition, for each predicted SHFT, the tables specify the dimension of the OP and the type of free-energy expansion associated with it. The detailed forms of these expansions are given in Table XI. The unit-cell multiplication which accompanies the transition, is determined by the translation symmetry properties of the OP and can be found in Table II of the present work for the cubic system and in Table II of TT for the other crystalline systems.

TABLE VI. Ferroelastoelectric transitions in the cubic system. All columns have the same content as Table IV.

High-symmetry space-group	BZ point	$\{\Gamma\}^2$	Ferroelastoelectric space-group	(a)	(b)
$Pm3$	Γ	all	$P23(\tau_5)$	1	a
	R		●		
	X		●		
	M		$I23(\tau_5,\tau_8)$, $I2_12(\tau_6,\tau_7)$	3	e
$Pn3$	Γ		$P23$	1	a
	R	all	●		
	X	●			
	M				
$Fm3$	Γ		$F23$	1	a
	X	all	$P23(\tau_5,\tau_7)$, $P2_13(\tau_6,\tau_8)$	3	e
	W	●			
	L	all	●		
$Fd3$	Γ		$F23$	1	a
	X	●			
	W				
	L	all	●		
$Im3$	Γ	all	$I23$	1	a
	H		●		
	N		$I23(\tau_3)$, $I2_13(\tau_4)$	6	h
	P	$\tau_2+\tau_3$ τ_1	●		
$Pa3$	Γ		$P2_13$	1	a
	R	all	●		
	X	●			
	M				
$Ia3$	Γ		$I2_13$	1	a
	H	all	●		
	N	●			
	P				
$P432$	Γ	τ_1,τ_2 τ_3	$P23(\tau_2)$	1	a
	R	τ_3	●		
	X	τ_1,τ_2	●		
	M	τ_3,τ_4	$I23(\tau_3)$, $I2_13(\tau_2)$	3	e
$F432$	Γ		$F23$	1	a
	X	τ_1,τ_2 τ_3,τ_4	$P23(\tau_2,\tau_3)$	3	e
	W	τ_1,τ_4	●		
	L	τ_1,τ_2	●		
$P4_232$	Γ		$P23$	1	a
	R	τ_3	●		
	X	τ_2,τ_3	●		
	M	τ_4,τ_5	$I2_13(\tau_3,\tau_4)$	3	e
$F4_132$	Γ		$F23$	1	a
	X	τ_2,τ_3 τ_4,τ_5	$P2_13(\tau_2,\tau_3)$	3	e
	W	●			
	L	τ_1,τ_2	$F23(\tau_1,\tau_2)$	4	f_2
$I432$	Γ		$I23$	1	a
	H	τ_3	●		
	N	all	$I23(\tau_4)$, $I2_13(\tau_3)$	6	h
	P	$\tau_2+\tau_3$ τ_1	●		
$P4_332$	Γ		$P2_13$	1	a
	R	●			
	X				
	M	all	●		
$P4_132$	Γ		$P2_13$	1	a
	R	●			
	X				
	M	all	●		
$I4_132$	Γ		$I2_13$	1	a
	H	τ_3	●		
	N	all	●		
	P	●			
$Pm3m$	Γ	all	$P\bar{4}3m(\tau_7)$	1	a
	R		●		
	X		●		
	M		$I\bar{4}3m(\tau_7,\tau_8)$ $I2_13(\tau_{10})$	3 6	e i
$Pn3n$	Γ		$P\bar{4}3n$	1	a
	R	$\tau_3+\tau_4$ τ_2	● ●		
	X	●			
	M	τ_1,τ_2	$I23(\tau_2)$	6	i
$Pm3n$	Γ		$P\bar{4}3n$	1	a
	R	$\tau_3+\tau_4$ τ_2	●		
	X	τ_3,τ_4	●		
	M	all	$I\bar{4}3d(\tau_7,\tau_{10})$ $I23(\tau_6)$	3 6	e i
$Pn3m$	Γ		$P\bar{4}3m$	1	a
	R	τ_3,τ_8	●		
	X	τ_3,τ_4	●		
	M		$I2_13(\tau_4)$	6	i
$Fm3m$	Γ		$F\bar{4}3m$	1	a
	X	all	$P\bar{4}3m(\tau_7,\tau_8)$ $P2_13(\tau_{10})$	3 6	e i
	W	τ_1,τ_2 τ_3,τ_4	●		
	L	all	●		
$Fm3c$	Γ		$F\bar{4}3c$	1	a
	X	all	$P\bar{4}3m(\tau_9)$, $P\bar{4}3n(\tau_6)$ $P2_13(\tau_{10})$	3 6	e i
	W	●			
	L				
$Fd3m$	Γ		$F\bar{4}3m$	1	a
	X	τ_3,τ_4	$P2_13(\tau_4)$	6	i
	W	●			
	L	all	$F\bar{4}3m(\tau_1,\tau_4)$, $F\bar{4}3c(\tau_2,\tau_5)$	4	f_2
$Fd3c$	Γ		$F\bar{4}3c$	1	a
	X	τ_3,τ_4	$P2_13(\tau_4)$	6	i
	W	●			
	L				
$Im3m$	Γ		$I\bar{4}3m$	1	a
	H	τ_3,τ_8	●		
	N	all	$I\bar{4}3m(\tau_8)$, $I\bar{4}3d(\tau_7)$	6	h
	P	τ_1,τ_2 τ_3	●		
$Ia3d$	Γ		$I\bar{4}3d$	1	a
	H	$\tau_3+\tau_4$ τ_2	●		
	N	●			
	P				

TABLE VII. Ferrobielastic transitions. The only BZ points indicated are those for which an FB transition is found possible. The results relative to the $\{\Gamma\}^2$ criterion can be found in Tables IV and V. Columns (a) and (b) have the same content as in Table IV.

High-symmetry space group	BZ point	Ferrobielastic space group	(a)	(b)
$P4/mmm$	Γ	$P4/m$	1	a
$P4/mcc$	Γ	$P4_2/m$	1	a
	A	$I4/m(\tau_1,\tau_2)$	2	b
	Z	$P4/m(\tau_1), P4_2/m(\tau_2)$	2	b
$P4/nbm$	Γ	$P4/n$	1	a
$P4/nnc$	Γ	$P4_2/n$	1	a
$P4/mbm$	Γ	$P4/m$	1	a
	M	$P4/m(\tau_1), P4/n(\tau_6)$	2	b
	A	$I4/m(\tau_1,\tau_6)$	2	b
$P4/mnc$	Γ	$P4/m$	1	a
	M	$P4/m(\tau_1), P4/n(\tau_6)$	2	b
	A	$I4/m(\tau_1,\tau_6)$	2	b
	R	$I4/m(\tau_1,\tau_2)$	4	g
$P4/nmm$	Γ	$P4/n$	1	a
$P4/ncc$	Γ	$P4/n$	1	a
$P4_2/mmc$	Γ	$P4_2/m$	1	a
$P4_2/mcm$	Γ	$P4_2/m$	1	a
$P4_2/nbc$	Γ	$P4_2/n$	1	a
$P4_2/nnm$	Γ	$P4_2/n$	1	a
$P4_2/mbc$	Γ	$P4_2/m$	1	a
	M	$P4_2/m(\tau_1), P4_2/n(\tau_6)$	2	b
$P4_2/mnm$	Γ	$P4_2/m$	1	a
	M	$P4_2/m(\tau_1), P4_2/n(\tau_6)$	2	b
	R	$I4_1/a(\tau_1,\tau_2)$	4	g
$P4_2/nmc$	Γ	$P4_2/n$	1	a
	A	$I4_1/a(\tau_1,\tau_2)$	2	b
$P4_2/ncm$	Γ	$P4_2/n$	1	a
	A	$I4_1/a(\tau_1,\tau_6)$	2	b
$I4/mmm$	Γ	$I4/m$	1	a
$I4/mcm$	Γ	$I4/m$	1	a
$I4_1/amd$	Γ	$I4_1/a$	1	a
$I4_1/acd$	Γ	$I4_1/a$	1	a
$P\bar{3}1m$	Γ	$P\bar{3}(\tau_2)$	1	a
	M	$P\bar{3}(\tau_2)$	3	e
$P\bar{3}1c$	Γ	$P\bar{3}$	1	a
	M	$P\bar{3}$	3	e
$P\bar{3}m1$	Γ	$P\bar{3}$	1	a
	M	$P\bar{3}$	3	e
$P\bar{3}c1$	Γ	$P\bar{3}$	1	a
	M	$P\bar{3}$	3	e
$R\bar{3}m$	Γ	$R\bar{3}$	1	a
	M	$R\bar{3}$	3	e
$R\bar{3}c$	Γ	$R\bar{3}$	1	a
	X	$R\bar{3}$	3	e
$P6/m$	Γ	$P\bar{3}(\tau_8)$	1	a
	M	$P\bar{3}(\tau_2)$	3	e
	K	$P\bar{3}(\tau_4)$	2	d
$P6_3/m$	Γ	$P\bar{3}$	1	a
	M	$P\bar{3}$	3	e
	K	$P\bar{3}$	2	d
$P6/mmm$	Γ	$P\bar{3}1m(\tau_4), P\bar{3}m1(\tau_3)$	1	a
	M	$P\bar{3}1m(\tau_2), P\bar{3}m1(\tau_3)$	3	e
	K	$P\bar{3}1m(\tau_4), P\bar{3}m1(\tau_5)$	2	d
$P6/mcc$	Γ	$P\bar{3}1c, P\bar{3}c1$	1	a
	M	$P\bar{3}1c, P\bar{3}c1$	3	e
	K	$P\bar{3}1c, P\bar{3}c1$	2	d
$P6_3/mcm$	Γ	$P\bar{3}1m, P\bar{3}c1$	1	a
	M	$P\bar{3}1m, P\bar{3}c1$	3	e
	K	$P\bar{3}1c, P\bar{3}m1$	2	d
$P6_3/mmc$	Γ	$P\bar{3}1c, P\bar{3}m1$	1	a
	M	$P\bar{3}1c, P\bar{3}m1$	3	e
	K	$P\bar{3}1m, P\bar{3}c1$	2	d

Let us clarify the use of the various tables by searching the possible SHFT arising from the high-symmetry phase $Fm3$. Table I shows that the $m3$ point group gives rise to a single secondary- or higher-order ferroic species, i.e., the FEE species $m3 \rightarrow 23$, characterized by the onset of the piezoelectric component $\pm d_{14}$. Referring to Table VI, dealing with FEE transitions of the cubic system, we find that for the $Fm3$ space group, FEE transitions are only possible at the Γ and X points of the BZ. The multidimensional IR at the W point are discarded because they do not fulfill the $\{\Gamma\}^2$ criterion, while the IR at the L point induce symmetry changes which are not FEE. At the Γ point, the (τ_5) one-dimensional representation determines the equitranslational symmetry change $Fm3 \rightarrow F23$.

At the X point, two possible transitions are predicted: $Fm3 \rightarrow P23$ and $Fm3 \rightarrow P2_13$. For both Table II indicates a fourfold expansion of the unit cell. The first symmetry change can be induced (Table VI) by two different IR identified by the small representations (τ_5) and (τ_7) of Zak's tables.[24] Likewise the second transition is induced by (τ_6) or (τ_8).

B. Predicted symmetry changes and experimental data

Newnham and Cross[12] have listed about 30 substances illustrating the various ferroic species. These substances can be divided into two groups.

The smaller group (Table XII) comprises crystals in which the existence of an SHFT is well established. This is, for instance, the case of the α-β transformation in quartz. For these crystals, structural and physical measurements are

TABLE VIII. Simultaneous ferroelastoelectric and ferrobielastic transitions in the tetragonal system. All columns have the same content as in Table IV.

High-symmetry space-group	BZ point	$\{\Gamma\}^2$	Ferroelastoelectric and Ferrobielastic space-group	(a)	(b)
$P4mm$	Γ	all	$P4(\tau_2)$	1	a
	M		●		
	Z		●		
	A		●		
	R		●		
	X		●		
$P4bm$	Γ		$P4$	1	a
	M	τ_1	$P4(\tau_1)$	2	b
	Z	all	●		
	A	τ_1	$I4(\tau_1)$	2	b
	R	●			
	X				
$P4_2cm$	Γ		$P4_2$	1	a
	M	all			
	Z	τ_1	$[P4_1, P4_31]\ (\tau_1)$	2	b
	A		$I4_1(\tau_1)$	2	b
	R	●			
	X	all	●		
$P4_2nm$	Γ		$P4_2$	1	a
	M	τ_1	$P4_2(\tau_1)$	2	b
	Z		$[P4_1, P4_31]\ (\tau_1)$	2	b
	A	all	●		
	R	●			
	X				
$P4cc$	Γ		$P4$	1	a
	M	all	●		
	Z	●			
	A				
	R				
	X	all	●		
$P4nc$	Γ		$P4$	1	a
	M	τ_1	$P4(\tau_1)$	2	b
	Z	●			
	A	τ_1	$I4(\tau_1)$	2	b
	R	●			
	X				
$P4_2mc$	Γ		$P4_2$	1	a
	M	all	●		
$P4_2mc$	Z	τ_1	$[P4_1, P4_3](\tau_1)$	2	b
	A	τ_1	$I4_1/a\,(\tau_1)$	2	b
	R	all	●		
	X		●		
$P4_2bc$	Γ		$P4_2$	1	a
	M	τ_1	$P4_2(\tau_1)$	2	b
	Z	τ_1	$[P4_1, P4_3](\tau_1)$	2	b
	A	●			
	R				
	X				
$I4mm$	Γ	all	$I4$	1	a
	Z		●		
	X		●		
	N		●		
	A		●		
$I4cm$	Γ		$I4$	1	a
	Z	all	●		
	X		●		
	N	●			
	A	●			
$I4_1md$	Γ		$I4_1$	1	a
	Z	τ_1	$[P4_1, P4_3](\tau_1)$	2	b
	X	●			
	N	all	●		
	A	●			
$I4_1cd$	Γ		$I4_1$	1	a
	Z	τ_1	$[P4_1, P4_3](\tau_1)$	2	b
	X	●			
	N				
	A				
$P\bar{4}2m$	Γ	all	$P\bar{4}(\tau_2)$	1	a
	M		●		
	Z		●		
	A		●		
	R		●		
	X		●		
$P\bar{4}2c$	Γ		$P\bar{4}$	1	a
	M	all	●		
	Z	$\tau_2+\tau_4$	●		
	A	$\tau_3+\tau_5$	●		
	R	all	●		
	X		●		
$P\bar{4}2_1m$	Γ		$P\bar{4}$	1	a
	M	all	$P\bar{4}(\tau_1)$	2	b
	Z		●		
	A		$I\bar{4}(\tau_1)$	2	b
	R	●			
	X				
$P\bar{4}2_1c$	Γ		$P\bar{4}$	1	a
	M	all	$P\bar{4}(\tau_1)$	2	b
	Z	$\tau_2+\tau_4$ $\tau_3+\tau_5$	●		
	A	all	$I\bar{4}(\tau_2+\tau_3, \tau_4+\tau_5)$	2	c
	R	●			
	X				
$P\bar{4}m2$	Γ	all	$P\bar{4}$	1	a
	M		●		
	Z		●		
	A		●		
	R		●		
	X		●		
$P\bar{4}c2$	Γ		$P\bar{4}$	1	a
	M	all	●		
	Z	$\tau_2+\tau_5$	●		
	A	$\tau_3+\tau_4$	●		
	R	●			
	X	all	●		
$P\bar{4}b2$	Γ		$P\bar{4}$	1	a
	M	$\tau_2+\tau_5$ $\tau_3+\tau_4$	●		
	Z	all	●		
	A	$\tau_2+\tau_5$ $\tau_3+\tau_4$	●		
	R	●			
	X				
$P\bar{4}n2$	Γ		$P\bar{4}$	1	a
	M	$\tau_2+\tau_5$	●		
	Z	$\tau_3+\tau_4$	●		
	A	all	●		
	R	●			
	X				
$I\bar{4}m2$	Γ		$I\bar{4}$	1	a
	Z		●		
	X		●		
	N		●		
	A	τ_1, τ_2	●		
$I\bar{4}c2$	Γ		$I\bar{4}$	1	a
	Z	all	●		
	X		●		
	N	●			
	A				
$I\bar{4}2m$	Γ	all	$I\bar{4}$	1	a
	Z		●		
	X		●		
	N		●		
	A	τ_1, τ_2 τ_3, τ_4	●		
$I\bar{4}2d$	Γ		$I\bar{4}$	1	a
	Z	$\tau_2+\tau_4$ $\tau_3+\tau_5$	●		
	X	●			
	N	all	$I\bar{4}(\tau_1, \tau_2)$	4	f_2
	A	●			
$4/mmm$ Class			No transitions to the $\bar{4}$ class		

generally available for both phases.

The second group (Table XIII) includes crystals in which no SHFT has been detected up to now. Also, the ferroic character is still speculative since no twinning has generally been reported. Newnham *et al.* have assigned ferroic properties to these compounds on the basis of the available structural data for a single phase. Each of the listed crystals possesses, besides its actual symmetry, a pseudosymmetry which can be attributed to a conjectured prototypic phase. The actual symmetry and the pseudosymmetry are such as to allow a classification of the considered crystal in one of the secondary- or higher-order ferroic species. In the former procedure, one uses implicitly a structural basis for ferroicity similar to that indicated by Abrahams and Keve[28] for ferroelectrics and ferroelastics. Following these authors, a crystal is recognized as a possible ferroic if pairs of atoms exist in its structure unrelated by the space group G of the crystal, and whose coordinates (x_1, y_1, z_1) and (x_2, y_2, z_2) can be related through transformations of the form

$$(x_2, y_2, z_2) = f(x_1, y_1, z_1) + \Delta(x_1, y_1, z_1)\,,$$

where f are space-symmetry operations not belonging to G, and Δ are small displacements of the order of 0.1 Å. The cancelling of these displacements will determine a phase with higher symmetry whose space group G_0 is obtained by combining G and all the above f operations.

At the experimental level, possible ferroic crystals can often be detected in the available x-ray data by the fact that an ambiguity remains on the actual symmetry of the crystal. This ambiguity can be induced in insufficiently precise measurements by the occurrence of the pseudosymmetry. It can also be determined by the presence of a great number of ferroic domains giving rise to the appearance of the average prototypic symmetry.

Let us now examine successively the theoretical results and the experimental data relative to the different types of SHFT.

1. *Ferroelastoelectric transitions*

In the orthorhombic system, most FEE transitions are predicted to occur at the BZ center (proper transitions—Table III). One exception is $Fddd \to F222$, arising at the R point of the BZ (F lattice). It corresponds to a four-dimensional OP and an eightfold expansion of the crystal's unit cell. In the tetragonal system, transitions are

TABLE IX. Simultaneous ferroelastoelectric and ferrobielastic transitions in the trigonal-hexagonal system. All columns have the same content as in Table V.

High-symmetry space-group	BZ point	$\{\Gamma\}^2$	Ferroelastoelectric and Ferrobielastic space-group	(a)	(b)
$P3m1$	Γ	all	$P3(\tau_2)$	1	a
	A		●		
	M		$P3(\tau_2)$	3	e
	L		●		
	H	τ_1	●		
	K		●		
$P31m$	Γ	all	$P3$	1	a
	A		●		
	M		$P3$	3	e
	L		●		
	H	●			
	K				
$P3c1$	Γ		$P3$	1	a
	A	●			
	M	all	$P3$	3	e
	L	●			
	H	●			
	K	τ_1	●		
$P31c$	Γ		$P3$	1	a
	A	●			
	M	all	$P3$	3	e
	L	●			
	H	●			
	K				
$R3m$	Γ	all	$R3(\tau_2)$	1	a
	Z		●		
	X		$R3(\tau_2)$	3	e
	A		●		
$R3c$	Γ		$R3$	1	a
	Z	●			
	X	all	$R3$	3	e
	A	●			
$P6$	Γ	τ_1, τ_2	$P3(\tau_2)$	1	a
	A				
	M	all	$P3(\tau_2)$	3	e
	L		●		
	H	τ_1	●		
	K		●		
$P6_1$	Γ		$P3_1$	1	a
	A	●			
	M	all	$P3_1$	3	e
	L	●			
	H	●			
	K	τ_1	●		
$P6_5$	Γ		$P3_2$	1	a
	A	●			
	M	all	$P3_2$	3	e
	L	●			
	H	●			
	K	τ_1	●		
$P6_2$	Γ		$P3_2$	1	a
	A	●			
	M	all	$P3_2$	3	e
	L		●		
	H	τ_1	●		
	K		●		
$P6_4$	Γ		$P3_1$	1	a
	A	●			
	M	all	$P3_1$	3	e
	L		●		
	H	τ_1	●		
	K		●		
$P6_3$	Γ		$P3$	1	a
	A	●			
	M	all	$P3$	3	e
	L	●			
	H	●			
	K	τ_1	●		
$P622$	Γ	τ_1, τ_2 τ_3, τ_4	$P321(\tau_3), P312(\tau_4)$	1	a
	A	●			
	M	all	$P321(\tau_2), P312(\tau_3)$	3	e
	L		●		
	H	τ_1, τ_2	●		
	K		$P321(\tau_2)$	2	d
$P6_122$	Γ		$P3_121, P3_112$	1	a
	A	●			
	M	all	$P3_121, P3_112$	3	e
	L	●			
	H	●			
	K	τ_1, τ_2	$P3_121$	2	d
$P6_522$	Γ		$P3_221, P3_212$	1	a
	A	●			
	M	all	$P3_221, P3_212$	3	e
	L	●			
	H	●			
	K	$\tau_1\tau_2$	$P3_221$	2	d
$P6_222$	Γ		$P3_221, P3_212$	1	a
	A	●			
	M	all	$P3_221, P3_212$	3	e
	L		●		
	H	$\tau_1\tau_2$	●		
	K		$P3_221$	2	d
$P6_422$	Γ		$P3_121, P3_112$	1	a
	A	●			
	M	all	$P3_121, P3_112$	3	e
	L		●		
	H	$\tau_1\tau_2$	●		
	K		$P3_121$	2	d
$P6_322$	Γ		$P321, P312$	1	a
	A	●			
	M	all	$P321, P312$	3	e
	L	●			
	H	●			
	K	$\tau_1\tau_2$	$P321$	2	d
$P6mm$	Γ		$P3m1(\tau_3), P31m(\tau_4)$	1	a
	M		$P3m1(\tau_4), P31m(\tau_2)$	3	e
	K		$P31m(\tau_2)$	2	d
$P6cc$	Γ		$P3c1, P31c$	1	a
	M		$P3c1, P31c$	3	e
	K		$P31c$	2	d
$P6_3cm$	Γ		$P3c1, P31m$	1	a
	M		$P3c1, P31m$	3	e
	K		$P31c$	2	d
$P6_3mc$	Γ		$P3m1, P31c$	1	a
	M		$P3m1, P31c$	3	e
	K		$P31m$	2	d
$P\bar{6}m2$	Γ		$P312(\tau_4)$	1	a
	M		$P312(\tau_3)$	3	e
	K		$P321(\tau_4)$	2	d
$P\bar{6}c2$	Γ		$P312$	1	a
	M		$P312$	3	e
	K		$P321$	2	d
$P\bar{6}2m$	Γ		$P321$	1	a
	M		$P321$	3	e
	K		$P312$	2	d
$P\bar{6}2c$	Γ		$P321$	1	a
	M		$P321$	3	e
	K		$P312$	2	d
$6/mmm$ class			No transitions towards the 32 class		

possible at several points of the BZ boundary (Table IV). Most of these improper FEE transitions involve a two-dimensional OP and a twofold expansion of the crystal's unit cell. Only two transitions, namely $I4_1/a \to I\bar{4}_1$ and $I4_1/amd \to (I\bar{4}m2, I\bar{4}c2)$ provide a more complex situation. They occur at the N point of the body-centered BZ and are associated with a fourdimensional OP and eightfold expansion of the unit cell.

In the trigonal-hexagonal system, FEE transi-

TABLE X. Higher-order ferroic transitions. For the $6/mmm$ and $m3m$ classes the results relative to the $\{\Gamma\}^2$ criterion can be found in Tables V and VI. In these two classes the only BZ points indicated in the tables are those for which an HOF transition is found possible. The $[\Gamma]^3$ column specifies the IR which do not fulfill the $[\Gamma]^3$ criterion and lead to discontinuous SHFT. Other columns have the same content as in Table IV.

High-symmetry space-group	BZ point	$\{\Gamma\}^2$	Higher-order ferroic space-group	(a)	(b)	$[\Gamma]^3$
$P6/mmm$	Γ		$P6/m(\tau_2)$	1	a	
	M		$P6/m(\tau_4)$	3	e	
	K		$P6/m(\tau_2)$	2	d	
$P6/mcc$	Γ		$P6/m$	1	a	
	M		$P6/m$	3	e	
	K		$P6/m$	2	d	
$P6_3/mcm$	Γ		$P6_3/m$	1	a	
	M		$P6_3/m$	3	e	
	K		$P6_3/m$	2	d	
$P6_3/mmc$	Γ		$P6_3/m$	1	a	
	M		$P6_3/m$	3	e	
	K		$P6_3/m$	2	d	
$P\bar{4}3m$	Γ	all	$P23(\tau_2)$	1	a	
	R	all	●			
	X	all	$P2_13(\tau_5)$	6	k	
	M	all	$I23(\tau_2, \tau_3)$,	3	e	
			$I2_13(\tau_5)$	6	i	τ_5
$F\bar{4}3m$	Γ		$F23$	1	a	
	X	all	$P23(\tau_2, \tau_3)$,	3	e	
			$P2_13(\tau_5)$	6	i	τ_5
	W	τ_1, τ_2	●			
	L	all	●			
$I\bar{4}3m$	Γ		$I23$	1	a	
	H	all	●			
	N	all	$I23(\tau_3), I2_13(\tau_4)$	6	h	
	P	τ_1, τ_2 τ_3	●			
$P\bar{4}3n$	Γ		$P23$	1	a	
	R	τ_3, $\tau_4 + \tau_5$	$F23(\tau_4 + \tau_5)$	2	c	
	X	$\tau_2 + \tau_4$ $\tau_3 + \tau_5$	$P2_13(\tau_2 + \tau_4, \tau_3 + \tau_5)$	6	m	
	M	all	$I2_13(\tau_3, \tau_4)$,	3	e	
			$I23(\tau_1)$	6	i	τ_1
$F\bar{4}3c$	Γ		$F23$	1	a	
	X	all	$P23(\tau_3, \tau_4)$,	3	e	
			$P2_13(\tau_1)$	6	i	τ_1
	W L	●				
$I\bar{4}3d$	Γ		$I2_13$	1	a	
	H	τ_3, $\tau_4 + \tau_5$	$P2_13(\tau_4 + \tau_5)$	2	c	
	N	●				
	P	$\tau_2 + \tau_3$	●			
$Pm3m$	Γ		$Pm3(\tau_2), P432(\tau_6)$	1	a	
	X		$Pa3(\tau_5, \tau_{10})$	6	k	
	M		$Im3(\tau_2, \tau_3), I432(\tau_6, \tau_9)$	3	e	
			$Ia3(\tau_5)$	6	i	τ_5
$Pn3n$	Γ		$Pn3, P432$	1	a	
	R		$[Fd3, F432](\tau_2)$	2	b	
	M		$I432(\tau_1)$	6	i	τ_1
$Pm3n$	Γ		$Pm3, P4_232$	1	a	
	R		$[Fm3, F4_132](\tau_2)$	2	b	
	X		$[Pa3, P4_132, P4_332](\tau_3, \tau_4)$	6	k	
	M		$Ia3(\tau_3, \tau_4), I4_132(\tau_8, \tau_9)$	3	e	
			$Im3(\tau 1)$	6	i	τ_1
$Pn3m$	Γ		$Pn3, P4_232$	1	a	
	X		$[P4_132, P4_332](\tau_3, \tau_4)$	6	k	
	M		$I4_132(\tau_3)$	6	i	τ_3
$Fm3m$	Γ		$Fm3, F432$	1	a	
	X		$Pm3(\tau_3), Pn3(\tau_2)$	3	e	
			$P432(\tau_6), P4_232(\tau_9)$	3	e	
			$Pa3(\tau_5)$	6	i	τ_5
$Fm3c$	Γ		$Fm3, F432$	1	a	
	X		$Pm3(\tau_3), Pn3(\tau_2)$	3	e	
			$P432(\tau_7), P4_232(\tau_8)$	3	e	
			$Pa3(\tau_5)$	6	i	τ_5
$Fd3m$	Γ		$Fd3, F4_132$	1	a	
	X		$\lvert P4_132, P4_332\rvert(\tau_3)$	6	i	τ_3
$Fd3c$	Γ		$Fd3, F4_132$	1	a	
	X		$[P4_132, P4_332](\tau_3)$	6	i	τ_3
$Im3m$	Γ		$Im3, I432$	1	a	
	N		$Im3(\tau_4), Ia3(\tau_3)$	6	h	
			$I432(\tau_5), I4_132(\tau_6)$	6	h	
$Ia3d$	Γ		$Ia3, I4_132$	1	a	
	H		$[Pa3, P432](\tau_2)$	2	b	

tions are possible for the Γ, K, and M points with, respectively, one-, two-, and three-dimensional OP (the unit cell is multiplied by one, three, and four).

In the cubic system, improper transitions are found at the M point of the simple cubic BZ, the X and L points of the face-centered lattice BZ, and at the N point of the body-centered lattice BZ. They correspond to three-, four-, and six-dimensional OP and to expansions of the unit cell by factors of 4 and 8.

In the latter system, a peculiar situation can be noted for the species $m3m \rightarrow 23$. As mentioned above, it involves a decrease of point symmetry by a factor of 4 which cannot be produced by a proper FEE transition. Table VI shows that this species can arise from improper transitions corresponding to the M point (P lattice) and the X point (F lattice). In both cases the transition has a six-dimensional OP and is accompanied by a fourfold expansion of the unit cell.

Two FEE species are associated with the $m3m$ prototypic group: $m3m \rightarrow \bar{4}3m$, and $m3m \rightarrow 23$. The preceding result shows that FEE transitions do not necessarily take place towards the larger of the two subgroups. This result can be compared to the case of ferroelectric transitions for which Ascher[29] has pointed out that the point-symmetry change was always towards the maximum polar subgroup of the paraelectric phase.

It is also remarkable that among the five species listed in Table I which involve a fourfold decrease of the point symmetry the species $m3m \rightarrow 23$ is the only one which can arise during a continuous phase transition.

Phase transitions with FEE symmetry change have been reported in ammonium chloride (NH_4Cl),[3] iron sulfide (FeS),[30] and cesium copper chloride ($CsCuCl_3$).[31]

NH_4Cl undergoes a FEE transition at −30 °C, with the symmetry change $Pm3m \rightarrow P\bar{4}3m$. This transition is nearly continuous and does not modify the number of atoms in the unit cell. Thus, it is a proper FEE transition which is induced, as shown by Table VI by the one-dimensional IR (τ_7) of the $m3m$ point group.

FeS provides an example of an improper FEE transition. This material transforms at 138 °C from $P\bar{6}2c$ to $P6_3/mmc$. This transition had been initially identified as a ferroelectric one.[32] This assignment is obviously incorrect since the low-symmetry group $\bar{6}2m$, though acentric, is nonpolar and thus incompatible with ferroelectricity.

X-ray measurements[33] have shown that a sixfold expansion of the unit cell accompanies the transition consisting in a doubling of the c parameter and in a threefold expansion in the (001) plane. Such a modification of the translational symmetry is related to the H point of the hexagonal BZ.[17] Table V indicates that for this point, no FEE transition is expected, due to the noncompatibility of the corresponding IR with the $\{\Gamma\}^2$ criterion. A further investigation shows that, nevertheless, the observed symmetry change can be induced by one of these IR, defined by a two-dimensional small representation (the OP is thus six dimensional). As discussed by several authors,[34] the nonfulfillment of the $\{\Gamma\}^2$ criterion should lead either to a spatially modulated structure for the $\bar{6}2m$ phase or to a first-order transition. This is consistent with experimental data which have detected a strong discontinuity and a large transition heat of 450 cal/mole.

$CsCuCl_3$ has been recently reported to experience the FEE symmetry change $P6_122 \rightarrow P6_3/mmc$ at about 150 °C.[31] An unusual feature of this transition is a threefold expansion of the c axis associated with the $(0, 0, 2\pi/3c)$ point located inside the first BZ of the high-symmetry phase. As emphasized in Sec. II, such a point is incompatible with the $\{\Gamma\}^2$ criterion. However, similarly to the preceding material, the transition in $CsCuCl_3$ is observed to be strongly discontinuous with a transition heat of 650 cal/mole.

A number of other substances have been pointed out by Newnham *et al.* as possible FEE (Table XIII). Some of these crystals provide potential examples for improper FEE.

Bismuth fluoride BiF_3 belongs to the same $P\bar{4}3m$ space group as the ferroic phase of ammonium chloride.[35] Its structure has the pseudosymmetry $Fm3m$ with a four times smaller primitive unit cell. The restoring of the higher symmetry would only require displacements of the Bi atoms by about 0.08 Å. A phase transition $P\bar{4}3m \rightarrow Fm3m$ is compatible with the predictions of Table VI. Such a symmetry change is induced by the (τ_7) or (τ_8) IR corresponding to the X point of the BZ (F lattice). It is described by a three-dimensional OP.

Other interesting examples are those indicated for the species $m3m \rightarrow 23$, namely, high crystobalite[35] (a high-temperature form of silica SiO_2), $KAlO_2$, and $KFeO_2$.[35] As mentioned above this species is necessarily associated with an improper transition.

The former three materials have been assigned the symmetry $P2_13$ and a pseudosymmetry $Fd3m$.[35] Table VI indicates the possibility of this symmetry change at the X point of the high-symmetry BZ. The transition would correspond to a six-dimensional OP and a fourfold expansion of the unit cell.

However a recent reexamination[36] of the structure of high crystoballite has case a doubt about the validity of the $P2_13$ space group. It appears

TABLE XI. Different types of free-energy expansions associated with SHFT. η, ζ, η_i are the different components of the OP. The β_i are temperature-independent coefficients, and $\alpha \approx T - T_c$. The expansions have been limited to the fourth-power terms except for (c) as the corresponding term has an isotropic symmetry and does not allow a discussion of the stability of the ferroic phase. Column 4 shows the polynomial of the OP, transforming according to the same one-dimensional IR of the BZ center, as the tensorial quantities characterizing the ferroic species.

Type of expansion	Quadratic term	Fourth- and higher-power terms	Symmetry of the spontaneous tensorial quantities	Secondary or higher order ferroic solutions	Stability conditions
a	$\frac{1}{2}\alpha\eta^2$	$\frac{1}{4}\beta\eta^4$	η	$\eta\neq 0$	$\beta>0$
b	$\frac{1}{2}\alpha(\eta^2+\zeta^2)$	$\frac{1}{4}\beta_1(\eta^4+\zeta^4)+\frac{1}{2}\beta_2\eta^2\zeta^2$	$\left\{\begin{matrix}\eta\zeta \text{ or}\\(\eta^2-\zeta^2)\end{matrix}\right.$	$\lvert\eta\rvert=\lvert\zeta\rvert$ or $\eta\neq 0 \quad \zeta=0$	$\left.\begin{matrix}\beta_1>\beta_2 \text{ or}\\ \beta_1<\beta_2\end{matrix}\right\}\beta_1>0$
c	$\frac{1}{2}\alpha(\eta^2+\zeta^2)$	$\left\{\begin{matrix}\frac{1}{4}\beta_1(\eta^4+\zeta^4)+\frac{1}{2}\beta_2\eta^2\zeta^2\\ +\beta_3\eta\zeta(\eta^2-\zeta^2)\end{matrix}\right.$	$\left\{\begin{matrix}\eta\zeta \text{ and}\\(\eta^2-\zeta^2)\end{matrix}\right.$	$\lvert\eta\rvert\neq\lvert\zeta\rvert$ and $\eta\neq 0 \quad \zeta\neq 0$	$\beta_1>0$
d	$\frac{1}{2}\alpha(\eta^2+\zeta^2)$	$\left\{\begin{matrix}\frac{1}{4}\beta(\eta^2+\zeta^2)^2+\frac{1}{6}(\gamma_1)(\eta^2+\zeta^2)^3\\ +\frac{1}{6}(\gamma_2)(\eta^2-\zeta^2)^3\end{matrix}\right.$	$\eta(\eta^2-3\zeta^2)$	$\eta\neq 0 \quad \zeta=0$	$\left\{\begin{matrix}\beta>0\\ \gamma_1>-\gamma_2>0\end{matrix}\right.$
e	$\frac{1}{2}\alpha\left(\sum_{j=1,3}\eta_j^2\right)$	$\left\{\begin{matrix}\frac{1}{4}\beta_1\left(\sum_{j=1,3}\eta_j^4\right)\\ +\frac{1}{2}\beta_2\left(\sum_{j<k=1,3}\eta_j^2\eta_k^2\right)\end{matrix}\right.$	$\eta_1\eta_2\eta_3$	$\lvert\eta_i\rvert=\lvert\eta_j\rvert\neq 0$	$\left\{\begin{matrix}\beta_1>0\\ \beta_1>\beta_2>-\beta_1\end{matrix}\right.$
f_1	$\frac{1}{2}\alpha\left(\sum_{j=1,4}\eta_j^2\right)$	$\left\{\begin{matrix}\frac{1}{4}\beta\left(\sum_{j=1,4}\eta_j^4\right)\\ +\frac{1}{2}\beta_2(\eta_1^2\eta_2^2+\eta_3^2\eta_4^2)\\ +\frac{1}{2}\beta_3(\eta_1^2\eta_3^2+\eta_2^2\eta_4^2)\\ +\frac{1}{2}\beta_4(\eta_1^2\eta_4^2+\eta_2^2\eta_3^2)\end{matrix}\right.$	$\eta_1\eta_2\eta_3\eta_4$	$\lvert\eta_i\rvert=\lvert\eta_j\rvert\neq 0$	$\beta_1>0$ $\beta_1+\beta_2+\beta_3+\beta_4>0$ $\beta_1>\beta_2+\beta_3+\beta_4$ $\beta_1+\beta_2>\beta_3+\beta_4$
f_2	$\frac{1}{2}\alpha\left(\sum_{j=1,4}\eta_j^2\right)$	$\left\{\begin{matrix}\frac{1}{4}\beta_1\left(\sum_{j=1,4}\eta_j^4\right)\\ +\frac{1}{2}\beta_2(\eta_1^2\eta_2^2+\eta_1^2\eta_4^2+\eta_2^2\eta_3^2+\eta_3^2\eta_4^2)\\ +\frac{1}{2}\beta_3(\eta_1^2\eta_3^2+\eta_2^2\eta_4^2)\end{matrix}\right.$	$\eta_1\eta_2\eta_3\eta_4$	$\lvert\eta_i\rvert=\lvert\eta_j\rvert\neq 0$	$\beta_1>0$ $\beta_1+2\beta_2+\beta_3>0$ $\beta_1>2\beta_2+\beta_3$ $\beta_1>\beta_3$
g	$\frac{1}{2}\alpha\left(\sum_{j=1,2}(\eta_j^2+\zeta_j^2)\right)$	$\left\{\begin{matrix}\frac{1}{4}\beta\left(\sum_{j=1,2}(\eta_j^4+\zeta_j^4)\right)\\ +\frac{1}{2}\beta_2\left(\sum_{j=1,2}\eta_j^2\zeta_j^2\right)\\ +\frac{1}{2}\beta_3(\eta_1^2\eta_2^2+\zeta_1^2\zeta_2^2+\eta_1^2\zeta_2^2+\eta_2^2\zeta_1^2)\end{matrix}\right.$ $+\beta_4\eta_1\eta_2\zeta_1\zeta_2$	$\eta_1\zeta_1+\eta_2\zeta_2$	$(\eta_1=\zeta_1)=\pm(\eta_2=\zeta_2)$	$\beta_1>0$ $\beta_1>\beta_4/2$ $\beta_1+\beta_2+\beta_4+2\beta_3>0$ $\beta_1+\beta_2>\beta_4+2\beta_3$

TABLE XI. *(Continued)*

Type of expansion	Quadratic term	Fourth- and higher-power terms	Symmetry of the spontaneous tensorial quantities	Secondary or higher order ferroic solutions	Stability conditions
h	$\frac{1}{2}\alpha\left(\sum_{j=1,6}\eta_j^2\right)$	$\frac{1}{4}\beta\left(\sum_{j=1,6}\eta_j^4\right)$ $+\frac{1}{2}\beta_2\left[\left(\sum_{j<k=1,6}\eta_j^2\eta_k^2\right)-(\eta_1^2\eta_4^2+\eta_2^2\eta_5^2+\eta_3^2\eta_6^2)\right]$ $+\frac{1}{2}\beta_3(\eta_1^2\eta_4^2+\eta_2^2\eta_5^2+\eta_3^2\eta_6^2)$ $+\beta_4(\eta_1\eta_2\eta_4\eta_5+\eta_1\eta_3\eta_4\eta_6+\eta_2\eta_3\eta_5\eta_6)$	$(\eta_1\eta_2\eta_6+\eta_1\eta_3\eta_5$ $+\eta_2\eta_3\eta_4+\eta_4\eta_5\eta_6)$	$(\eta_1=\eta_4)$ $=\pm(\eta_2=\eta_5)$ $=\pm(\eta_3=\eta_6)$	$\beta_1>0$ $\beta_1+4\beta_2+\beta_3+2\beta_4>0$ $\beta_1>\beta_4$ $\beta_1+\beta_3>2\beta_2+\beta_4$
i	$\frac{1}{2}\alpha\left(\sum_{j=1,3}(\eta_j^2+\zeta_j^2)\right)$	$\frac{1}{4}\beta_1\left(\sum_{j=1,3}(\eta_j^4+\zeta_j^4)\right)$ $+\frac{1}{2}\beta_2\left(\sum_{j<1,3}(\eta_j^2\eta_k^2+\zeta_j^2\zeta_k^2)\right)$ $+\frac{1}{2}\beta_3\left(\sum_{j=1,3}\eta_j^2\zeta_j^2\right)$ $+\frac{1}{2}\beta_4\left(\sum_{i\neq j=1,3}\eta_i^2\zeta_j^2\right)$	$\sum_{j=1,3}(\eta_j^2-\zeta_j^2)$ and $\eta_1\eta_2\eta_3+\zeta_1\zeta_2\zeta_3$ and $\eta_1\eta_2\eta_3-\zeta_1\zeta_2\zeta_3$	$\|\eta_i\|=\|\eta_j\|\neq 0$ $\zeta_i=0$	$\beta_1>0$ $\beta_1+2\beta_2>0$ $\beta_1>\beta_2$ $\beta_3+2\beta_4>\beta_1+2\beta_2$
k	Same terms as (i)	Same terms as (i)	$\sum_{j=1,3}(\eta_j^2-\zeta_j^2)$ or $\sum_{j=1,3}\eta_j\zeta_j$	$\|\eta_i\|=\|\eta_j\|\neq 0$ $\zeta_k=0$ $\|\eta_i\|=\|\eta_j\|=\|\zeta_k\|$	Same as (i) or $\beta_1>0$ $\beta_1+2\beta_2+\beta_3+2\beta_4>0$ $\beta_1>\beta_2$ $\beta_1+2\beta_2>\beta_3+2\beta_4$
m	Same terms as (i)	Same terms as (i) $+\beta_5\left(\sum_{j=1,3}\eta_j\zeta_j\right)\times\left(\sum_{j=1,3}(\eta_j^2-\zeta_j^2)\right)$	$\sum_{j=1,3}(\eta_j^2-\zeta_j^2)$ and $\sum_{j=1,3}\eta_j\zeta_j$	$(\|\eta_i\|=\|\eta_j\|)\neq$ $(\|\zeta_i\|=\|\zeta_j\|)$	$\beta_1>0$

that SiO_2 has a disordered structure with average space-group $Fd3m$, the local structure being tetragonal. Thus, only $KAlO_2$ and $KFeO_2$ remain as possible illustrations of the anomalous $m3m \rightarrow 23$ species.

2. *Ferrobielastic transitions*

As shown by Table VII, both proper and improper FB transitions are found possible. For most of them the OP symmetries are similar to those encountered for FEE transitions. However, a new situation can be pointed out for the R point of the simple tetragonal BZ. It concerns the symmetry changes $P4/mnc \rightarrow I4/m$ and $P4_2/mnm \rightarrow I4_1/a$, and involves a four-dimensional OP and a fourfold expansion of the unit cell.

Lanthanum cobalt oxide $LaCoO_3$ undergoes the FB symmetry change $R\bar{3}c \rightarrow R\bar{3}$ at 375 °C.[37] This crystal has the high-symmetry phase stable below the transition's temperature, in contrast to the more usual situation.

Precise x ray measurements[37] have detected no modification of the translational symmetry. Thus this material is an example of proper FB, whose symmetry change is consistent with the results of Table VII. Three other speculative FB with proper transitions are indicated on Table XIII.

Niobium dioxide displays a more complex and interesting situation. At room temperature, NbO_2 possesses a distorted rutile structure. Single-crystal x-ray measurements by Marinder[38] have assigned to it the space group $I4_1/a$, with a primitive unit cell eight-times larger than that of rutile, whose space group is $P4_2/mnm$. On the other hand, powder x-ray measurements have been performed by Sakata *et al.*,[39] showing that the rutile structure is restored at high temperature. A phase transition has been detected by these authors near 800 °C through anomalies in the thermal expansion of the material. More recently, neutron scattering measurements by Shapiro *et al.*[2] have confirmed the occurrence of a transition at 808 °C. The temperature dependence of the observed reflection intensities could be interpreted satisfactorily by these authors, assuming that the eightfold expansion of the unit cell takes place at this transition, and is induced by an IR corresponding to the $\vec{k}$ vector $(\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$ lying *inside* the first BZ of the $P4_2/mnm$ group. An unpublished group-theoretical calculation quoted by Mukamel[20] further shows that the space-group change $P4_2/mnm \rightarrow I4_1/a$ can be induced by a one-dimensional small representation associated with the above $\vec{k}$ vector, whose star has four arms (the OP is therefore four dimensional). We have checked the latter statement and found it correct. However, as

TABLE XII. Materials possessing a secondary ferroic transition. The dimension of the corresponding OP is indicated as well as its translational symmetry (BZ point) and the corresponding unit cell expansion occuring at the transition. "Yes" or "no" in the $\{\Gamma\}^2$ column means that the $\{\Gamma\}^2$ criterion is or is not satisfied by the IR which induces the transition. I and P in the column "nature of the transition" mean "improper" and "proper", respectively.

Ferroic type	Material	Space-group change	T_c (K)	Nature of the transition	OP dimension	Unit-cell expansion	BZ point	$\{\Gamma\}^2$	Reference
FEE	FeS	$P6_3/mmc \rightarrow P\bar{6}2c$	410	I	6	6	H	No	30
	$CsCuCl_3$	$P6_3/mmc \rightarrow P6_122$	423	I	...	3	Inside	No	31
	NH_4Cl	$Pm3m \rightarrow P\bar{4}3m$	243	P	1	1	Γ	Yes	3
FB	NbO_2	$P4_2/mnm \rightarrow I4_1/a$	1080	I	4	8	Inside	No	2
		$P4_2/mnm \rightarrow P4_2/m \rightarrow I4_1/a$	1080–1150	I	2; 2	2; 4	M; R	Yes	This work
	$LaCoO_3$	$R\bar{3}c \rightarrow R\bar{3}$	648	P	1	1	Γ	Yes	37
FEE and FB	SiO_2	$P6_{2,4}22 \rightarrow P3_{1,2}21$	846	P	1	1	Γ	Yes	1
	$AlPO_4$	$P6_{2,4}22 \rightarrow P3_{1,2}21$	852	P	1	1	Γ	Yes	40

TABLE XIII. Materials which constitute possible ferroics. The space group of the prototypic phase coincides with the one describing the pseudosymmetry of the structure.[35] Column Δ: maximum atomic displacements involved between the actual structure and the prototypic one. The other columns have the same meaning as in Table XII.

Ferroic type	Material	Speculative prototypic space group	Ferroic space group	Δ (Å)	Nature of the transition	OP dimension	Unit-cell expansion	BZ point
FEE	PNb_9O_{25}	$I4/m$	$I\bar{4}$	···	P	1	1	Γ
	$CuCr_2O_4$	$I4_1/amd$	$I\bar{4}2d$	0.2	P	1	1	Γ
	$Cs_3As_2Cl_9$	$P\bar{3}m1$	$P321$	0.15	P	1	1	Γ
	N_2	$Pa3$	$P2_13$	0.17	P	1	1	Γ
	$KAlO_2$	$Fd3m$	$P2_13$	···	I	6	4	X
	BiF_3	$Fm3m$	$P\bar{4}3m$	0.08	I	3	4	X
FB	$K_2OsO_2(OH)_4$	$I4/mmm$	$I4/m$	0.25	P	1	1	Γ
	AsI_3	$R\bar{3}c$	$R\bar{3}$	0.0	P	1	1	Γ
	$FeSiF_6\cdot 6H_2O$	$R\bar{3}m$	$R\bar{3}$	a	P	1	1	Γ
FEE and FB	Na_2ThF_6	$P\bar{6}2m$	$P321$	0.4	P	1	1	Γ
Higher order	$K_3W_2Cl_9$	$P6_3/mmc$	$P6_3/m$	0.2	P	1	1	Γ
	K_2NaAlF_6	$Fm3m$	$Pa3$	b	I	6	4	X
	$N_2H_6Cl_2$	$Fm3m$	$Pa3$	0.2	I	6	4	X

[a] For $FeSiF_6\cdot 6H_2O$ the occurence of two stable states with average symmetry $R\bar{3}m$ has actually been detected by x-ray measurements.

[b] The conjectured mechanism of a transition is of the order-disorder type and would not involve atomic displacements.

already stressed by Mukamel,[20] it appears that the considered IR does not satisfy the $\{\Gamma\}^2$ criterion.

By contrast to the case of FeS and $CsCuCl_3$, the transition in NbO_2 is of second thermodynamic order.[2] Besides no spatial modulation of the room-temperature phase has been detected from x-ray or neutron scattering measurements. Consequently, this transition complies strictly with the applicability conditions of the Landau theory, and the noncompliance to the $\{\Gamma\}^2$ criterion appears as a serious drawback of the interpretation of Shapiro *et al.* A reexamination of the existing x-ray work,[39] in the light of the present theoretical results, allows us to propose an alternate interpretation of the experimental data which, moreover, preserves the validity of the Landau symmetry criteria.

Sakata *et al.*[39] have observed that in their powder x-ray data the superlattice reflections related to the distortion of the rutile structure disappear between 850 and 900 °C, some 75 °C higher than the temperature of the anomalies of the material's thermal expansion (797 °C). The latter temperature is close to the transition temperature indicated by Shapiro *et al.*[2] for the neutron scattering data (808 °C) and should be identified with it.

On the basis of the x-ray results, we can therefore assume that two successive phase transitions are present in NbO_2, one in the range 850–900 °C, and the other near 800 °C, the space-group above 900 °C being that of rutile ($P4_2/mnm$). In this model, the translational symmetry is expected to decrease in two steps with a modification of the Bravais lattice following one of two schemes: $P \rightarrow P \rightarrow I$ or $P \rightarrow I \rightarrow I$. By examing the Bravais lattice changes[17] associated with the various high-symmetry points of the tetragonal BZ boundary, it is found that only the first scheme can account for the observed modification of translational symmetry. For this scheme two possibilities can be considered:

$P \rightarrow P$ (M point of the BZ), then $P \rightarrow I$ (R point);

$P \rightarrow P$ (X point), then $P \rightarrow I$ (A point).

Reference to Table IV permits one to rule out the second sequence, as transitions are forbidden by the $\{\Gamma\}^2$ criterion at the X point of the $P4_2/mnm$ space group. Therefore a single possibility remains corresponding to the sequence of transitions:

$$P4_2/mnm \rightarrow P4_2/m \rightarrow I4_1/a\,.$$

The first transition is induced by a two-dimensional IR (τ_1) at the M point of the BZ of $P4_2/mnm$ (Table VII). It involves a twofold expansion of the unit cell. The translations of the low- and high-symmetry phases are related by

$$\vec{a}_1' = \vec{a}_1^0 - \vec{a}_2^0, \quad \vec{a}_2' = \vec{a}_1^0 + \vec{a}_2^0, \quad \vec{a}_3' = \vec{a}_3^0\,.$$

The second transition is a mere change of translational symmetry induced by a two-dimensional IR (a real one-dimensional τ_n and a two-arm star) corresponding to the R point of the simple tetragonal BZ. The final body-centered tetragonal cell is

$$\vec{a}_1 = 2(\vec{a}_1^0 - \vec{a}_2^0), \quad \vec{a}_2 = 2(\vec{a}_1^0 + \vec{a}_2^0), \quad \vec{a}_3 = 2\vec{a}_3^0.$$

This cell coincides with that of the room-temperature phase of NbO_2.[38] The preceding model thus accounts for the space group and primitive translations of NbO_2, as well as for the temperature dependence of the x-ray powder spectra. It also explains the neutron scattering data if a relabelling of the observed reflections is performed in order to refer these reflections to the BZ of the intermediate $P4_2/m$ phase, and not to that of the $P4_2/mnm$ phase. The reflection assigned to the wave vector $(\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$ has to be relabelled $(0, \frac{1}{2}, \frac{1}{2})$ and thus corresponds to the R point of the BZ which is associated by the present interpretation with the 800 °C transition. Likewise the reflections at $(\frac{1}{2}, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, 0)$ must be relabelled $(\frac{1}{2}, \frac{1}{2}, 0)$ and $(0, 1, 0)$. The proportionality pointed out by Shapiro *et al.* between the intensity of the two latter reflections and the square of the intensity of the former one is obviously consistent with our interpretation as well, since this proportionality relies on a geometrical relation between the $\vec{k}$ vectors which is not modified by the former relabelling.

A consequence of the conjectured mechanism is that the 808 °C transition possesses a two-dimensional OP instead of the four-dimensional OP assumed by Mukamel.[18] Accurate single-crystal x-ray measurements between 800 and 900 °C should decide between the two interpretations.

3. Simultaneously ferroelastoelectric and ferrobielastic transitions

Tables VIII and IX indicate that the types of OP symmetries are the same as for FEE transitions.

The α-β transformation of quartz (SiO_2) is an example of both a proper FEE and FB transition. This transformation occurs at 573 °C with the space-group change $P3_121 \rightarrow P6_422$. Its thermodynamic order is close to second order[1] (slightly first order). The primitive translations are the same for both phases. The symmetry change is thus consistent with that predicted for the Γ point of the BZ of the high-symmetry space group. $AlPO_4$ is isostructural with quartz and undergoes an identical transition at 579 °C.[40]

Two other materials are suggested by Newnham *et al.*[12] as possible FEE and FB. However, one of them, Ag_2HgI_4, involves very large displacements of the silver atoms to achieve the prototypic structure,[35] and is therefore unlikely to be a ferroic. The pseudosymmetry of the other one,[35] Na_2ThF_6, permits classification as a proper ferroic. No example for an improper FEE and FB transition is available.

4. Higher-order ferroic transitions

Two differences can be pointed out between the results for HOF transitions (Table X) and those relative to the FEE transitions of the cubic system (Table VI).

In the first place several HOF transitions are found possible at the X point of the simple cubic BZ; they correspond to a six-dimensional OP and an eightfold expansion of the unit cell of the crystal.

On the other hand, the six-dimensional IR at the M points of the P Brillouin zone and at the X point of the F Brillouin zone do not satisfy the $[\Gamma]^3$ criterion. They are associated with discontinuous transitions falling outside the scope of this work. Nevertheless, we have indicated the corresponding symmetry change (Table X), as these IR constitute the only exceptions of the cubic system with respect to the $[\Gamma]^3$ criterion. This does not imply that the tables also account for possible first-order transitions, as these transitions can arise, for instance, when the symmetry of the OP is described by a reducible representation of the prototypic phase, a circumstance not considered here.

No phase transition of the HOF type has yet been experimentally reported. Three compounds can however be considered as possible examples (Table XIII).

The structure of $K_3W_2Cl_9$ has the symmetry $P6_3/m$ and a pseudosymmetry $P6_3/mmc$.[35] The prototypic and ferroic unit cells have the same number of atoms. The symmetry change is consistent with a proper transition indicated in Table X for the Γ point of the high-symmetry group.

$N_2H_6Cl_2$ possesses a structure ($Pa3$) slightly distorted with respect to that of CaF_2 ($Fm3m$).[35] The modification of the Bravais lattice between the distorted and prototypic structures discloses the improper character of the corresponding HOF transition. This symmetry change is in agreement with the indications of Table X at the X point of the BZ (F lattice). The OP is six dimensional and the transition is predicted to be first order.

The same symmetry change $Fm3m \rightarrow Pa3$ is conjectured for elpasolite K_2NaAlF_6.[12] However, as shown in detail by Newnham *et al.*, the mechanism of a transition in this material would involve an order-disorder process rather than the displacement of certain atoms: the $Fm3m$ space group corresponds to the random occupation of unequivalent sites in the cell by the potassium and sodium atoms, while the ordered pattern is described by the $Pa3$ group.

Elspasolite belongs to the cryolite[41] family in which several transitions with a ferroelastic symmetry change have been reported by x-ray measurements. Up to 500 °C no transition was detected in K_2NaAlF_6. However, the expected transition, though first order, leaves the crystal in the cubic system and might have been difficult to detect through powder x-ray experiments.

C. Free-energy expansions associated with the SHFT

The form of the expansion associated with a transition depends on the form of the set of matrices representing the IR which induces the symmetry change.[22] In the case of the investigated SHFT, twelve different forms of expansions were encountered. They are listed in Table XI. They correspond to one-, two-, three-, four-, and six-dimensional OP. To each OP dimension are associated one or several types of expansions which are distinguished by the expression of the various fourth-power invariants, by the faintness index, and by the form of the OP contribution to the mixed invariant, defined in Sec. II.

It is well known[14] that several low-symmetry phases are compatible with a multidimensional IR. Each one is associated with a set of relative values for the components of the OP. Table XI specifies the set corresponding to a secondary- or higher-order ferroic phase as well as the conditions imposed on the β_i coefficients of the expansion in order to insure that this set of OP values determines an absolute minimum for the free-energy expansion. It appears that, for all the SHFT indicated in Tables III–X, there exists a range of compatible β_i coefficients corresponding to the stability of the considered ferroic phase.

The inequalities which determine the suitable range of β_i values have been established without taking into account in the expansion the mixed invariant. The effect of such a term can be to change the thermodynamic order of the transition from second to first.[15,16,42] We assumed that the coefficient of the mixed invariant was sufficiently small to make the influence of this term negligible.

It has been pointed out in Sec. II that the mixed invariant term depends linearly on the tensorial components characterizing the considered ferroic species. Each of these tensorial components transforms according to a one-dimensional IR of the prototypic point group. Consequently, the OP contribution to the mixed invariant is a polynomial transforming according to the same IR. This IR is also the one which induces a proper transition for the considered species. For instance, if we consider the FEE transition $Pm3m \rightarrow I\bar{4}3m$ described by the expansion labelled (e) in Table XI, the OP contribution to the mixed invariant is $\eta_1\eta_2\eta_3$, which transforms in the same way as the piezoelectric modulus d_{14} according to the (τ_7) IR of the $m3m$ point group (Table VI).

The case of the species $m3m \rightarrow 23$ is more complex since there is no IR of the $m3m$ point group related to it. The corresponding improper transitions are described by an expansion labelled (i) in Table XI, for which three OP contributions to the mixed invariant are indicated:

$$\sum_{j=1,3} (\eta_j^2 - \zeta_j^2), \quad \eta_1\eta_2\eta_3 + \zeta_1\zeta_2\zeta_3, \quad \eta_1\eta_2\eta_3 - \zeta_1\zeta_2\zeta_3 .$$

These three terms transform according to the (τ_7), (τ_2), and (τ_6) one-dimensional IR of the $m3m$ point group, respectively, related to the species $m3m \rightarrow \bar{4}3m$, $m3m \rightarrow m3$, and $m3m \rightarrow 432$. The three terms are simultaneously nonzero for the set of OP values:

$$|\eta_1| = |\eta_2| = |\eta_3| \neq 0 \quad \text{and} \quad \zeta_i = 0 .$$

The preceding values correspond to a phase whose point symmetry is the intersection of $\bar{4}3m$, $m3$, and 432, that is, the 23 point group.

We can note that in most of the other transitions, the OP can also couple in a similar way to several IR of the prototypic point group. However, the OP contribution to all the mixed invariants other than the one indicated in Table XI vanish for the set of OP values corresponding to the SHFT.

For instance, the OP of the $Pm3m \rightarrow I\bar{4}3m$ transition mentioned above can couple to a two-dimensional IR of the $m3m$ point group by means of the set of polynomials

$$(2\eta_1^2 - \eta_2^2 - \eta_3^2, \ 2\eta_2^2 - \eta_1^2 - \eta_3^2) .$$

It is clear that the corresponding mixed invariant will vanish for the set of values $|\eta_1| = |\eta_2| = |\eta_3|$ relevant to the transition $Pm3m \rightarrow I\bar{4}3m$ (Table XI).

Hence, the uniqueness of the $m3m \rightarrow 23$ transition among all the investigated SHFT is related to the fact that three mixed invariants corresponding to different point-symmetry changes can be simultaneously nonzero for a stable state of the crystal.

An expansion similar to (i), which has also been labelled (i) in Table X, occurs for several discontinuous HOF transitions. It has in common with (i) the second- and fourth-power terms. In addition, it possesses a third-power invariant equal to one of the two terms $(\eta_1\eta_2\eta_3 + \zeta_1\zeta_2\zeta_3)$ or $(\eta_1\eta_2\eta_3 - \zeta_1\zeta_2\zeta_3)$. The OP contribution to the mixed invariant is

$$\sum_{j=1,3} (\eta_j^2 - \zeta_j^2) .$$

This expansion has not been reproduced in Table XI.

IV. CONCLUSION

The main usefulness of the present work consists in a tabulation of the results obtained by a systematic examination of the irreducible representations of 147 space groups. The tables indicate all the space-group changes relative to secondary- or higher-order ferroic species which are compatible with the Landau theory of continuous phase transitions. Their consultation allows a straightforward determination of the dimension and symmetry properties of the order parameter corresponding to a given space-group change, as well as the derivation of the associated free-energy expansion. The tables presented here are complementary to those worked out in TT[17]; these two studies exhaust all the ferroic transitions which keep unchanged the crystalline system, i.e., all those which are nonferroelastic.

The present results demonstrate that both proper and improper SHFT are possible. The latter transitions are associated with two-, three-, four, and six-dimensional order parameters. The complexity of these transitions is thus greater than that of the previously investigated ferroelectric nonferroelastic transitions,[17] where only two-, and three-dimensional order parameters were found.

A peculiar situation has been pointed out for the ferroelastoelectric species $m3m \rightarrow 23$. This species, as well as four others, involves a decrease of the number of point-symmetry elements by a factor of 4, and its occurrence is forbidden at the Brillouin-zone center. However, by contrast to the other four species, which are also forbidden at other BZ points, a continuous transition $m3m \rightarrow 23$ has been found to be possible at the BZ boundary. This prediction is in agreement with the experimental data, since examples have been indicated for the species $m3m \rightarrow 23$, while none is available for the four other mentioned species.

Crystals which constitute proven or speculative examples for SHFT have been examined with respect to their order-parameter symmetries. Proper as well as improper transitions were identified in the available materials, in agreement with the tables.

In the case of two crystals possessing an SHFT of the improper type, namely FeS and $CsCuCl_3$, it was noted that the irreducible representations describing the symmetry change do not fulfill the $\{\Gamma\}^2$ symmetry criterion. However, these materials undergo strongly discontinuous transitions, and therefore escape the strict application of the Landau's theory.

In a third crystal, NbO_2, the current interpretation of the 800 °C phase transition also implied an incompatibility with the $\{\Gamma\}^2$ rule. We have stressed that this crystal poses a serious challenge to the validity of the Landau's theory as its transition is continuous and does not give rise to a spatially modulated structure. By using the tables established here, we have been able to show that an alternate interpretation, preserving the validity of the $\{\Gamma\}^2$ rule, could be given of the experimental data for NbO_2. It assumes the occurrence of two successive transitions, one at 800 °C and the other between 800 and 900 °C. As a consequence, the 800 °C transition is predicted to be described by a two-dimensional order parameter instead of the four-dimensional one assumed up to now.

FeS and $CsCuCl_3$ are two of the three examples in which an SHFT of the improper type is confirmed at present. The interpretations of their transitions denotes the nonfulfillment of the $\{\Gamma\}^2$ criterion. The same situation was pointed out in TT for the only two available examples of improper ferroelectric nonferroelastic transitions, i.e., $(NH_4)_2BeF_4$ and $NaH_3(SeO_3)_2$. It is puzzling to note that most actual examples of improper transitions which preserve the crystalline system (i.e., nonferroelastic) seem to contradict the $\{\Gamma\}^2$ symmetry criterion, while most improper transitions which involve a modification of the crystalline system (ferroelastic) respect this rule.[43-46]

---

[1] J. P. Bachheimer and G. Dolino, Phys. Rev. B 11, 3195 (1975).

[2] S. M. Shapiro, J. D. Axe, G. Shirane, and P. M. Raccah, Solid State Commun. 15, 377 (1974).

[3] C. H. Wang and R. B. Wright, J. Chem. Phys. 60, 849 (1974).

[4] F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon, New York, 1962).

[5] K. Aizu, J. Phys. Soc. Jpn. 27, 387 (1969).

[6] Proceedings of the Third European Meeting on Ferroelectricity, Ferroelectrics (Gordon and Breach, London, 1976), Vols. 12–14.

[7] L. A. Thomas and W. A. Wooster, Proc. R. Soc. A 208, 43 (1951).

[8] K. Aizu, J. Phys. Soc. Jpn. 34, 121 (1973).

[9] V. L. Indenbom, Kristallografyia 5, 115 (1960) [Sov. Phys.-Crystallogr. 5, 106 (1960)].

[10] The possibility of a polarization reversal does not exist at room temperature in several well-known substances, such as lithium niobate or barium sodium niobate which are, nevertheless, classified among ferroelectrics.

[11] J. F. Nye, *Physical Properties of Crystals* (Clarendon, Oxford, 1960).

[12] R. E. Newnham and L. E. Cross, Mater. Res. Bull. 9, 927 (1974); 9, 1021 (1974); Ferroelectrics 10, 269 (1976); R. E. Newnham, Am. Mineral. 59, 906 (1974).

[13] We can discard, for instance, from secondary ferroics, ferrobielectrics (Ref. 12), in which ΔF is a quadratic function of the electric field, as the corresponding crystallographic species are identical to the ferroelastic ones. They can therefore be considered from a symmetry point of view as primary ferroics.

[14] L. D. Landau and E. M. Lifschitz, *Statistical Physics* (Addison-Wesley, Reading, Mass., 1958).

[15] A. P. Levanyuk and D. G. Sannikov, Usp. Fiz. Nauk 112, 561 (1974) [Sov. Phys.-Usp. 17, 199 (1975)].

[16] V. Dvorak, Ferroelectrics 7, 1 (1974).

[17] P. Toledano and J. C. Toledano, Phys. Rev. B 14, 3097 (1976).

[18] D. Mukamel, Phys. Rev. Lett. 34, 481 (1975).

[19] K. G. Wilson and J. Kogut, Phys. Rep. 12, 75 (1974).

[20] D. Mukamel and S. Krinsky, Phys. Rev. B 13, 5065 (1976).

[21] This definition does not hold for ferroelastics different ferroelastic species can correspond to the same set of point groups (Ref. 5).

[22] G. Ya. Lyubarskii, *The Application of Group Theory in Physics* (Pergamon, New York, 1960).

[23] C. J. Bradley and A. P. Cracknell, *The Mathematical Theory of Symmetry in Solids* (Clarendon, Oxford, 1972).

[24] J. Zak, A. Casher, H. Glück, and Y. Gur, *The Irreducible Representations of Space Groups* (Benjamin, New York, 1969).

[25] J. Birman, Phys. Rev. Lett. 17, 1216 (1966).

[26] O. V. Kovalev, Irreducible Representations of Space Groups (Gordon and Breach, New York, 1965).

[27] V. Janovec, V. Dvořak, and J. Petzelt, Czech. J. Phys. B 25, 1362 (1975).

[28] S. C. Abrahams and E. T. Keve, Ferroelectrics 2, 129 (1971).

[29] E. Ascher, Phys. Lett. 20, 352 (1966).

[30] M. G. Townsend, J. R. Gosselin, R. J. Tremblay, and and A. H. Webster, J. Phys. (Paris) Suppl. 10, C4-11 (1976).

[31] S. Hirotsu, J. Phys. C 8, L12 (1975).

[32] C. B. Van den Berg, J. E. Van Delden, and J. Bouman, Phys. Status Solidi 36, K 89 (1969).

[33] E. F. Bertaut, Bull. Sci. Fr. Mineral. Cristallogr. 79, 276 (1956).

[34] V. Dvorak, Phys. Status Solidi B 66, K 87 (1974).

[35] R. W. G. Wyckoff, *Crystal Structures* (Interscience, New York, 1960), Vols. 1–3.

[36] A. F. Wright and A. J. Leadbetter, Philos. Mag. 31, 1391 (1975).

[37] P. M. Raccah and J. P. Goodenough, Phys. Rev. 155, 932 (1967).

[38] B. O. Marinder, Ark. Kemi 19, 435 (1962).

[39] T. Sakata, K. Sakata, and I. Nishida, Phys. Status Solidi 20, K 155 (1967).

[40] R. Lang, W. R. Datars, and C. Calvo, Phys. Lett. A 30, 340 (1969).

[41] E. G. Steward and H. P. Rooksby, Acta. Crystallogr. 6, 49 (1953).

[42] V. Dvořak, Phys. Status Solidi B 45, 147 (1971).

[43] J. C. Toledano, Ann. Telecommun. 29, 249 (1974).

[44] J. Torres, Phys. Status Solidi B 71, 141 (1975).

[45] J. C. Toledano, Phys. Rev. B 12, 943 (1975).

[46] W. Prettl and K. H. Rieder, Phys. Rev. B 14, 2171 (1976).