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Nonferroic phase transitions

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Nonferroic phase transitions are defined as the structural transitions occurring with a breaking of translational symmetry within the same crystal class. They involve no new macroscopic tensor components below the transition point, and they are generally identified experimentally through the onset of superlattice reflections denoting the multiplication of the crystal's unit cell. A theoretical analysis of these transitions is presented, based on Landau's symmetry criteria for continuous transitons, of the order-parameter symmetries, space-group changes, and free-energy expansions. We establish that the order parameters of such transitions are necessarily related to one-dimensional (real or complex) small representations of the group of the $\vec{k}$ vector. Their symmetry characteristics are, in general, simpler than those of other types of structural transitions. Most of them possess a one-component order parameter inducing a doubling of the unit cell. The remaining ones are associated with order-parameter dimensions as high as six, and unit-cell multiplications up to thirty-two. The coupling of the order parameter to macroscopic quantities, illustrated by the example of dielectric ones, is shown to belong to two possible schemes. The relation between nonferroics and antiferroelectrics is discussed. The theoretical results are compared to the available experimental data which pertain mainly to organic compounds and metallic alloys.

I. INTRODUCTION

The onset of spontaneous, symmetry-breaking, macroscopic quantities (i.e., polarization, strain) during a crystalline phase transition involves necessarily a modification of the crystal's point group. This circumstance is encountered in most of the well-known categories of structural phase transitions such as ferroelectric and ferroelastic ones. It has led Aizu to define the concept of a ferroic crystal[1] which covers besides the two preceding extensively studied groups of transitions, more complex ones characterized by the onset of spontaneous tensorial quantities of rank higher than 2.[2] Various authors[1–3] have listed the orientational symmetry changes ("ferroic species") relative to the various types of ferroic phase transitions.

However, substances have long been known, which undergo a crystalline transition without the advent of any point symmetry breaking, but solely with a decreasing of the translational symmetry. These transitions will not involve any spontaneous macroscopic component. By reference to Aizu's terminology we can call them "nonferroic phase transitions" (NFPT). The change of translational symmetry distinguishes NFPT's from the so-called[4] isomorphous phase transitions which occur without any modification of the crystal's symmetry.

The experimental identification of a NFPT proceeds mainly through the detection, below the transition, of superlattice reflections denoting the multiplication of the number of atoms in the crystal's unit cell. The available experimental results show that these transitions are also accompanied by anomalies in the dielectric or the elastic properties.

A number of organic compounds display a NFPT, for instance chloranil[5] $C_6Cl_4O_2$, fluoronaphthalene[6] $C_{10}F_8$ and NN-dimethylnitramine.[7] Several insulating mineral compounds are also known, such as potassium cyanide KCN (Ref. 8) and cesium trihydrogen selenite[9] $CsH_3(SeO_3)_2$, as well as entire structural families of metallic alloys, for example the groups labeled $B2$ and $L1_2$.[10] This relative abundance of illustrative examples is surprising, because the experimental identifications of NFPT's should have been hampered by the lack of new tensorial components below the transition point. It suggests that the considered class of transitions is very commonly realized in nature. This has stimulated us to undertake its theoretical analysis in order to specify its distinctive aspects and to evaluate its importance among the structural transitions which are predicted to be possible in the framework of Landau's theory of continuous phase transitions.[11]

On the basis of this theory, we establish, in Sec. II, a theorem which restricts drastically the types of irreducible representations of the crystallographic space groups that are likely to induce a nonferroic symmetry change. This result simplifies the systematic working out of the order-parameter symmetries, space-group changes and free-energy expansions of possible NFPT's. In this section, the preceding characteristics are summarized in table form, and compared to previous crystallographic works.

Section III is devoted to a detailed examination of the experimental data. In Sec. IV, attention is given to the forms of the free energies and to the coupling of the order parameter to macroscopic quantities. In particular, we discuss the dielectric anomalies which are expected to occur at a NFPT.

II. THEORETICAL PROCEDURE AND RESULTS

The method used to apply the Landau theory to continuous NFPT's is identical to that previously used for ferroic phase transitions[12–14] and described in detail in these references. It involves three steps. In the first place, the "active"[15] irreducible representations (IR) of each of the 230 crystallographic space-groups (SG), denoted G_0, are selected on the basis of the Landau[11] and Lifschitz[15] symmetry criteria. This selection determines a few stars k^* in the Brillouin zone (BZ) of G_0, and certain small representations[15] τ_n of the group $G_{\vec{k}}$ of the $\vec{k}$-vector representative of k^*. The free-energy expansion associated to the IR is then constructed and its minima specified as a function of the expansion's coefficients. Finally the symmetry change $G_0 \rightarrow G$ corresponding to each minimum, is worked out.

NFPT's possess specific characteristics which simplify significantly the general procedure. The simplifications are based on the following theorem: A NFPT can only be induced by an IR whose small representation τ_n is one dimensional (real or complex). Let us establish this property.

(i) Let G_0 and G be the SG of the high- and low-symmetry phases and $G_{\vec{k}}$ the invariance space group of the $\vec{k}$-vector representative of the star k^*

TABLE I. NFPT's in the triclinic and monoclinic systems. The detailed meaning of the columns is explained in the Appendix.

(a)	(b)	(c)	(d)	(e)	(f)
P1	ABY	$P1(\tau_1)$	2	1	a
	ZED				
$P\bar{1}$	C	$P\bar{1}(\tau_1,\tau_2)$			
P2	Z	$P2(\tau_1),P2_1(\tau_2)$	2	1	a
	ABY	$P2(\tau_1,\tau_2)$			
	EDC	$B2(\tau_1,\tau_2)$			
$P2_1$	ABY	$P2_1(\tau_1,\tau_2)$			
B2	ZA	$P2(\tau_1),P2_1(\tau_2)$			
	BYC	$B2(\tau_1,\tau_2)$			
	FF"	$B2(\tau_1)$	4	2	b
Pm	Z	$Pm(\tau_1,\tau_2)$	2	1	a
	ABY	$Pm(\tau_1),Pb(\tau_2)$			
	EDC	$Bm(\tau_1,\tau_2)$			
Pb	ZY	$Pb(\tau_1,\tau_2)$			
	C	$Bb(\tau_1,\tau_2)$			
Bm	ZA	$Pm(\tau_1),Pb(\tau_2)$			
	BYC	$Bm(\tau_1),Bb(\tau_2)$			
	FF"	$Bm(\tau_1)$	4	2	b
Bb	ZA	$Pb(\tau_1,\tau_2)$	2	1	a
	FF"	$Bb(\tau_1)$	4	2	b
P2/m	Z	$P2/m(\tau_1,\tau_3),P2_1/m(\tau_2,\tau_4)$	2	1	a
	ABY	$P2/m(\tau_1,\tau_4),P2/b(\tau_2,\tau_3)$			
	EDC	$B2/m(\tau_1 \rightarrow \tau_4)$			
$P2_1/m$	ABY	$P2_1/m(\tau_1,\tau_4),P2_1/b(\tau_2,\tau_3)$			
B2/m	ZA	$P2/m(\tau_1)$, $P2_1/b(\tau_2)$ $P2/b(\tau_3)$, $P2_1/m(\tau_4)$			
	BYC	$B2/m(\tau_1,\tau_4)$, $B2/b(\tau_2,\tau_3)$			
	FF"	$B2/m(\tau_1,\tau_2)$	4	2	b
P2/b	Z	$P2/b(\tau_1,\tau_3)$, $P2_1/b(\tau_2,\tau_4)$	2	1	a
	A	$P2/b(\tau_1 \rightarrow \tau_4)$			
	E	$B2/b(\tau_1 \rightarrow \tau_4)$			
$P2_1/b$	A	$P2_1/b(\tau_1 \rightarrow \tau_4)$			
B2/b	ZA	$P2/b(\tau_1,\tau_3)$, $P2_1/b(\tau_2,\tau_4)$			
	FF"	$B2/b(\tau_1,\tau_2)$	4	2	b

associated to the considered IR ($G_{\vec{k}} \subset G_0$). We note $\hat{G}_0$, $\hat{G}$, and $\hat{G}_{\vec{k}}$ the corresponding point groups. G is defined[11] as the invariance group of the function

$$\delta\rho = \sum_{\vec{k}} \sum_{n} C_{\vec{k},n} \Phi_n(\vec{k}) \ , \qquad (1)$$

where $\vec{k}$ and n, respectively, run over the arms of k^* and the basis of the small IR, τ_n. The set of $\phi_n(\vec{k})$ is assumed to be a standard[15] basis of the IR.

As for a NFPT $\hat{G} = \hat{G}_0$, G will necessarily include the operations which transform $\vec{k}$ into any other arm $\vec{k}'$, of the star k^*. As the basis of the IR is chosen in

TABLE II. NFPT's in the orthorhombic system.

(a)	(b)	(c)	(d)	(e)	(f)
$P222$	Z	$P222(\tau_1,\tau_4)$, $P222_1(\tau_2,\tau_3)$	2	1	a
	X	$P222(\tau_1,\tau_2)$, $P222_1(\tau_3,\tau_4)$			
	Y	$P222(\tau_1,\tau_3)$, $P222_1(\tau_2,\tau_4)$			
	TUS	$C222(\tau_1 \rightarrow \tau_4)$			
	R	$F222(\tau_1 \rightarrow \tau_4)$			
$P222_1$	X	$P222_1(\tau_1,\tau_2)$, $P2_12_12(\tau_3,\tau_4)$			
	Y	$P222_1(\tau_1,\tau_3)$, $P2_12_12(\tau_2,\tau_4)$			
	S	$C222_1(\tau_1 \rightarrow \tau_4)$			
$P2_12_12$	Z	$P2_12_12(\tau_1,\tau_4)$, $P2_12_12_1(\tau_2,\tau_3)$			
$C222_1$	Y	$P222_1(\tau_1)$, $P2_12_12(\tau_2,\tau_3)$ $P2_12_12_1(\tau_4)$			
	S	$C222_1(\tau_1,\tau_2)$	4	2	b
$C222$	Y	$P222_1(\tau_1)$, $P2_12_12(\tau_2,\tau_3)$ $P2_12_12_1(\tau_4)$	2	1	a
	Z	$C222(\tau_1,\tau_4)$, $C222_1(\tau_2,\tau_3)$			
	T	$I222(\tau_1,\tau_4)$, $I2_12_12_1(\tau_2,\tau_3)$			
	S	$C222(\tau_1,\tau_2)$	4	2	b
	R	$F222(\tau_1,\tau_2)$			
$F222$	XYZ	$C222(\tau_1,\tau_4)$, $C222_1(\tau_2,\tau_3)$	2	1	a
	T	$C222(\tau_1,\tau_2)$, $C222_1(\tau_3,\tau_4)$			
	R	$(F222,F222)(\tau_1)$	8	4	f_5
$I222$	X	$P222(\tau_1)$, $P2_12_12(\tau_2,\tau_3,\tau_4)$	2	1	a
	TUS	$C222(\tau_1,\tau_2)$	4	2	b
	R	$F222(\tau_1 \rightarrow \tau_4)$	4	2	c
$I2_12_12_1$	X	$P2_12_12_1(\tau_1)$, $P222_1(\tau_2,\tau_3,\tau_4)$	2	1	a
	TUS	$C222_1(\tau_1,\tau_2)$	4	2	b
$Pmm2$	Z	$Pmm2(\tau_1)$, $Pmc2_1(\tau_2,\tau_4)$, $Pcc2(\tau_3)$			
	X	$Pmm2(\tau_1,\tau_4)$, $Pma2(\tau_2,\tau_3)$			
	Y	$Pmm2(\tau_1,\tau_2)$, $Pma2(\tau_3,\tau_4)$	2	1	a
	T	$Amm2(\tau_1,\tau_2)$, $Ama2(\tau_3,\tau_4)$			
	U	$Amm2(\tau_1,\tau_4)$, $Ama2(\tau_2,\tau_3)$			
	S	$Cmm2(\tau_1 \rightarrow \tau_4)$			
	R	$Fmm2(\tau_1 \rightarrow \tau_4)$			
$Pmc2_1$	X	$Pmc2_1(\tau_1,\tau_4)$, $Pmn2_1(\tau_2,\tau_3)$			
	Y	$Pmc2_1(\tau_1,\tau_2)$, $Pca2_1(\tau_3,\tau_4)$			
	S	$Cmc2_1(\tau_1 \rightarrow \tau_4)$			
$Pcc2$	X	$Pcc2(\tau_1,\tau_4)$, $Pnc2(\tau_2,\tau_3)$			
	Y	$Pcc2(\tau_1,\tau_2)$, $Pnc2(\tau_3,\tau_4)$			
	S	$Ccc2(\tau_1 \rightarrow \tau_4)$			
$Pma2$	Z	$Pma2(\tau_1)$, $Pmn2_1(\tau_2)$ $Pnc2(\tau_3)$, $Pca2_1(\tau_4)$			
	Y	$Pma2(\tau_1,\tau_2)$, $Pba2(\tau_3,\tau_4)$			
	T	$Ama2(\tau_1,\tau_2)$, $Aba2(\tau_3,\tau_4)$			
$Pca2_1$	Y	$Pca2_1(\tau_1,\tau_2)$, $Pna2_1(\tau_3,\tau_4)$	2	1	a
$Pnc2$	X	$Pnc2(\tau_1,\tau_4)$, $Pnn2(\tau_2,\tau_3)$			
$Pmn2_1$	Y	$Pmn2_1(\tau_1,\tau_2)$, $Pna2_1(\tau_3,\tau_4)$			
$Pba2$	Z	$Pba2(\tau_1)$, $Pna2_1(\tau_2,\tau_4)$, $Pnn2(\tau_3)$			
$Pnn2$	R	$Fdd2\ (\tau_1 \rightarrow \tau_4)$			
$Cmm2$	Y	$Pmm2(\tau_1)$, $Pma2(\tau_2,\tau_4)$, $Pba2(\tau_3)$			
	Z	$Cmm2(\tau_1)$, $Cmc2_1(\tau_2,\tau_3)$, $Ccc2(\tau_4)$			
	T	$Imm2(\tau_1)$, $Ima2(\tau_2,\tau_4)$, $Iba2(\tau_3)$			
	S	$Cmm2(\tau_1,\tau_2)$	4	2	b
	R	$Fmm2(\tau_1,\tau_2)$			
$Cmc2_1$	Y	$Pmc2_1(\tau_1)$, $Pmn2_1(\tau_2)$, $Pna2_1(\tau_3)$, $Pca2_1(\tau_4)$	2	1	a
	S	$Cmc2_1(\tau_1,\tau_2)$	4	2	b
$Ccc2$	Y	$Pcc2(\tau_1)$, $Pnc2(\tau_2,\tau_4)$, $Pnn2(\tau_3)$	2	1	a
	S	$Ccc2(\tau_1,\tau_2)$	4	2	b
	R	$Fdd2(\tau_1,\tau_2)$			
$Amm2$	Y	$Pmm2(\tau_1)$, $Pmc2_1(\tau_2)$, $Pnc2(\tau_3)$, $Pmn2_1(\tau_4)$	2	1	a
	Z	$Amm2(\tau_1,\tau_2)$, $Abm2(\tau_3,\tau_4)$			
	T	$Imm2(\tau_1,\tau_2)$, $Ima2(\tau_3,\tau_4)$			
	S	$Amm2(\tau_1)$, $Abm2(\tau_2)$	4	2	b
	R	$Fmm2(\tau_1,\tau_2)$			
$Abm2$	Y	$Pma2(\tau_1)$, $Pca2_1(\tau_2)$, $Pcc2(\tau_3)$, $Pmc2_1(\tau_4)$	2	1	a
	Z	$Abm2(\tau_1,\tau_2)$, $Aba2(\tau_3,\tau_4)$			
	T	$Iba2(\tau_1,\tau_2)$, $Ima2(\tau_3,\tau_4)$			
$Ama2$	Y	$Pma2(\tau_1)$, $Pca2_1(\tau_2)$, $Pcc2(\tau_3)$, $Pmc2_1(\tau_4)$			
	S	$Ama2(\tau_1)$, $Aba2(\tau_2)$	4	2	b
	R	$Fdd2(\tau_1,\tau_2)$			
$Aba2$	Y	$Pba2(\tau_1)$, $Pca2_1(\tau_2)$, $Pnc2(\tau_3)$, $Pna2_1(\tau_4)$	2	1	a
$Fmm2$	XY	$Amm2(\tau_1)$, $Abm2(\tau_2)$, $Aba2(\tau_3)$, $Ama2(\tau_4)$	2	1	a
	ZT	$Cmm2(\tau_1)$, $Cmc2_1(\tau_2,\tau_4)$, $Ccc2(\tau_3)$			
	R	$(Fmm2,Fdd2)(\tau_1)$	8	4	f_5
$Imm2$	X	$Pmm2(\tau_1)$, $Pmn2_1(\tau_2,\tau_4)$, $Pnn2(\tau_3)$	2	1	a
	TU	$Amm2(\tau_1)$, $Abm2(\tau_2)$	4	2	b
	S	$Cmm2(\tau_1,\tau_2)$			
	R	$(Fmm2,Fdd2)(\tau_1,\tau_2)$			
$Iba2$	X	$Pcc2(\tau_1)$, $Pca2_1(\tau_2,\tau_4)$, $Pba2(\tau_3)$	2	1	a
	S	$Ccc2(\tau_1,\tau_2)$	4	2	b
$Ima2$	X	$Pma2(\tau_1)$, $Pmc2_1(\tau_2)$, $Pnc2(\tau_3)$, $Pna2_1(\tau_4)$	2	1	a
	T	$Ama2(\tau_1)$, $Aba2(\tau_2)$	4	2	b
	S	$Cmc2_1(\tau_1,\tau_2)$	4	2	b

TABLE II (*Continued*).

(a)	(b)	(c)	(d)	(e)	(f)
Pmmm	X	Pmmm(τ_1,τ_6), Pccm(τ_2,τ_5), Pmma$(\tau_3,\tau_4,\tau_7,\tau_8)$	2	1	a
	Y	Pmmm(τ_1,τ_7), Pccm(τ_3,τ_5), Pmma$(\tau_2,\tau_4,\tau_6,\tau_8)$			
	Z	Pmmm(τ_1,τ_8), Pccm(τ_4,τ_5), Pmma$(\tau_2,\tau_3,\tau_6,\tau_7)$			
	T	Cmmm$(\tau_1,\tau_2,\tau_7,\tau_8)$, Cmma$(\tau_3,\tau_4,\tau_5,\tau_6)$			
	U	Cmmm$(\tau_1,\tau_3,\tau_6,\tau_8)$, Cmma$(\tau_2,\tau_4,\tau_5,\tau_7)$			
	S	Cmmm$(\tau_1,\tau_4,\tau_6,\tau_7)$, Cmma$(\tau_2,\tau_3,\tau_5,\tau_8)$			
	R	Fmmm$(\tau_1 \rightarrow \tau_8)$			
Pnnn	R	Fddd$(\tau_1 \rightarrow \tau_8)$			
Pccm	X	Pccm(τ_1,τ_6), Pban(τ_2,τ_5), Pcca(τ_3,τ_8), Pmna(τ_4,τ_7)			
	Y	Pccm(τ_1,τ_7), Pban(τ_2,τ_8), Pcca(τ_3,τ_5), Pmna(τ_4,τ_6)			
	S	Cccm$(\tau_1,\tau_4,\tau_6,\tau_7)$, Ccca$(\tau_2,\tau_3,\tau_5,\tau_8)$			
Pban	Z	Pban(τ_1,τ_8), Pnna$(\tau_2,\tau_3,\tau_6,\tau_7)$, Pnnn$(\tau_4,\tau_5)$			
Pmma	Y	Pmma(τ_1,τ_7), Pbcm(τ_2,τ_8),Pmna(τ_3,τ_5), Pmmn(τ_4,τ_8)			
	Z	Pmma(τ_1,τ_8), Pbcm(τ_2,τ_7), Pbam(τ_3,τ_6), Pcca(τ_4,τ_5)			
	T	Cmcm$(\tau_1,\tau_2,\tau_7,\tau_8)$, Cmca$(\tau_3,\tau_4,\tau_5,\tau_6)$			
Pmna	Y	Pmna(τ_1,τ_4), Pnnm(τ_2,τ_8), Pnna(τ_3,τ_5), Pbcn(τ_4,τ_6)			
Pcca	Y	Pcca(τ_1,τ_7), Pccn(τ_2,τ_8), Pnna(τ_3,τ_5), Pbcn(τ_4,τ_6)			
Pbam	Z	Pbam(τ_1,τ_8), Pnma$(\tau_2,\tau_3,\tau_6,\tau_7)$, Pnnm$(\tau_4,\tau_5)$			
Pbcm	X	Pbcm(τ_1,τ_6), Pbcn(τ_2,τ_5), Pbca(τ_3,τ_8), Pnma(τ_4,τ_5)			
Pmmn	Z	Pmmn(τ_1,τ_8) Pnma$(\tau_2,\tau_3,\tau_6,\tau_7)$, Pccn$(\tau_4,\tau_5)$			
Cmcm	Y	Pmma(τ_1), Pnnm(τ_2), Pbcn(τ_3), Pnma(τ_4,τ_8) Pnna(τ_5), Pbcm(τ_6), Pmmn(τ_7)			
	S	Cmcm$(\tau_1.\tau_4)$, Cmca(τ_2,τ_3)	4	2	b
Cmca	Y	Pbam$(\tau.)$, Pmna(τ_2), Pbca(τ_3), Pccn(τ_4) Pbcn(τ_5), Pcca(τ_6), Pnma(τ_7), Pbcm(τ_8)	2	1	a
Cmmm	Y	Pmmm(τ_1), Pmna(τ_2,τ_3), Pbam(τ_4) Pban(τ_5), Pmma(τ_6,τ_7), Pmmn(τ_8)	2	1	a
	Z	Cmmm(τ_1,τ_8), Cmcm$(\tau_2,\tau_3,\tau_6,\tau_7)$, Cccm$(\tau_4,\tau_5)$			
	T	Immm(τ_1,τ_8), Imma$(\tau_2,\tau_3,\tau_6,\tau_7)$, Ibam$(\tau_4,\tau_5)$			
	S	Cmmm(τ_1,τ_4), Cmma(τ_2,τ_3)	4	2	b
	R	Fmmm$(\tau_1 \rightarrow \tau_4)$			
Cccm	Y	Pccm(τ_1), Pnna(τ_2,τ_3), Pnnm(τ_4) Pnnn(τ_5), Pmna(τ_6,τ_7), Pccn(τ_8)	2	1	a
	S	Cccm(τ_1,τ_4), Ccca(τ_2,τ_3)	4	2	b
	R	Fddd$(\tau_1 \rightarrow \tau_4)$			
Cmma	Y	Pccm(τ_1,τ_5), Pmma(τ_2,τ_7), Pcca(τ_3,τ_6), Pbcm(τ_4,τ_8)	2	1	a
	Z	Cmma(τ_1,τ_8), Cmca$(\tau_2,\tau_3,\tau_6,\tau_7)$, Ccca$(\tau_4,\tau_5)$			
	T	Ibam(τ_1,τ_8), Imma(τ_2,τ_7), Ibca$(\tau_3,\tau_4,\tau_5,\tau_6)$			
Ccca	Y	Pban(τ_1,τ_5), Pnna(τ_2,τ_7), Pcca(τ_3,τ_6), Pbcn(τ_4,τ_8)			
Fmmm	XT	Cmmm(τ_1), Cmma(τ_2), Cmca$(\tau_3,\tau4)$ Ccca(τ_5), Cmcm(τ_6,τ_8), Cccm(τ_7)			
	Y	Cmmm(τ_1), Cmca(τ_2,τ_4), Cmma(τ_3) Ccca(τ_5), Cmcm(τ_6,τ_7), Cccm(τ_8)			
	Z	Cmmm(τ_1), Cmca(τ_2,τ_8), Cmma(τ_3) Cccm(τ_4), Ccca(τ_5), Cmcm(τ_6,τ_7)			
	R	Fmmm(τ_1), Fddd(τ_2)	8	4	f_5
Immm	X	Pmmm(τ_1), Pnnm(τ_2,τ_3,τ_4), Pnnn(τ_5), Pmmn(τ_6,τ_7,τ_8)	2	1	a
	TUS	Cmmm(τ_1,τ_4), Cmma(τ_2,τ_3)	4	2	b
	R	(Fmmm, Fddd)$(\tau_1 \rightarrow \tau_4)$			
Ibam	X	Pccm(τ_1), Pbcn(τ_2,τ_3), Pbam(τ_4) Pban(τ_5), Pbcm(τ_6,τ_7), Pccn(τ_8)	2	1	a
	S	Cccm(τ_1,τ_4), Ccca(τ_2,τ_3)	4	2	b
Ibca	X	Pbca(τ_1,τ_5), Pcca$(\tau_2,\tau_3,\tau_4,\tau_6,\tau_7,\tau_8)$	2	1	a
Imma	X	Pmma(τ_1,τ_8), Pmna$(\tau2,\tau_6)$, Pnma(τ_3,τ_7), Pnna(τ_4,τ_5)			
	TU	Cmcm(τ_1,τ_4), Cmca(τ_2,τ_3)	4	2	b

the standard way,[15] an operation of G transforming $\vec{k}$ into $\vec{k}'$, will also transform $\Phi_n(\vec{k})$ into $\Phi_n(\vec{k}')$ (same index n). The invariance of $\delta\rho$ by this operation imposes that $C_{\vec{k},n}$ is independent of $\vec{k}$:

$$C_{\vec{k},n}=C_{\vec{k}',n} \ . \tag{2}$$

Thus $\delta\rho$ can be written as

$$\delta\rho=\sum_n C_n\left[\sum_{\vec{k}}\Phi_n(\vec{k})\right] \ , \tag{3}$$

one coefficient C_n at least being nonzero in the low-symmetry phase.

(ii) Let H be the set of elements common to G and $G_{\vec{k}}$

$$H=G\cap G_{\vec{k}} \ . \tag{4}$$

H is a subgroup of $G_{\vec{k}}$; so we can write

$$G_{\vec{k}}=g_1H+g_2H+\cdots \ . \tag{5}$$

As $\hat{G}=\hat{G}_0$, we have also $\hat{G}_{\vec{k}}=\hat{H}$: $G_{\vec{k}}$ and H have the same point-group operations, and $g_1,g_2,\ldots$ are necessarily pure translations which belong to $G_{\vec{k}}$ but not to H. (The g_i are in fact the translations lost in the transition from G_0 to G.)

Thus we can write

$$g=\{E\,|\,\vec{t}\}h \quad (g\in G_{\vec{k}},\ \ h\in H) \ , \tag{6}$$

$\{E\,|\,\vec{t}\}$ being a pure translation.[16]

(iii) Let us consider the function

$$\delta\rho_{\vec{k}}=\sum_n C_n\phi_n(\vec{k}) \ , \tag{7}$$

with the $\phi_n(\vec{k})$ spanning τ_n. Like $G_{\vec{k}}$, H leaves $\vec{k}$ unchanged. Thus each of its elements do not only preserve $\delta\rho$ as a whole but also its $\vec{k}$ contribution $\delta\rho_{\vec{k}}$:

$$h(\delta\rho_{\vec{k}})=\delta\rho_{\vec{k}} \quad (h\subset H) \ . \tag{8}$$

Using (6) we then find

$$g\delta\rho_{\vec{k}} = \{E\,|\,\vec{t}\}\delta\rho_{\vec{k}} = e^{i\vec{k}\cdot\vec{t}}\delta\rho_{\vec{k}}\ . \qquad (9)$$

The action of an element of $G_{\vec{k}}$ on the function $\delta\rho_{\vec{k}}$ leads to a multiplication of $\delta\rho_{\vec{k}}$ by a scalar. Thus $\delta\rho_{\vec{k}}$ spans a one-dimensional representation of $G_{\vec{k}}$ contained in τ_n. As τ_n is irreducible, we conclude that it is one dimensional itself.

The previous theorem allows to discard from the present study all the IR's whose small representation is multidimensional. On the other hand, it gives a

TABLE III. NFPT's in the tetragonal system.

(a)	(b)	(c)	(d)	(e)	(f)
P4	Z	$P4(\tau_1)$, $P4_2(\tau_2)$	2	1	a
	MX	$P4(\tau_1,\tau_2)$	2,4	1,2	a,b
	AR	$I4(\tau_1,\tau_2)$			
$P4_1$	MX	$P4_1(\tau_1,\tau_2)$	2,4	1,2	a,b
$P4_2$	Z	$P4_1(\tau_3)$, $P4_3(\tau_4)$	2	1	a
	MX	$P4_2(\tau_1,\tau_2)$	2,4	1,2	a,b
	A	$I4_1(\tau_3,\tau_4)$	2	1	a
	R	$I4_1(\tau_1,\tau_2)$	4	2	b
$P4_3$	MX	$P4_3(\tau_1,\tau_2)$	2,4	1,2	a,b
I4	MZX	$P4(\tau_1)$,$P4_2(\tau_2)$	2,2,4	1,1,2	a,a,b
	A	$(I4,I4_1)(\tau_1)$	4	2	b
	N	$I4_1(\tau_1)$	8	4	f_4
$I4_1$	MZX	$P4_1(\tau_1)$, $P4_3(\tau_2)$	2,2,4	1,1,2	a,a,b
$P\bar{4}$	ZMX	$P\bar{4}(\tau_1,\tau_2)$	2,2,4	1,1,2	a,a,b
	AR	$I\bar{4}(\tau_1,\tau_2)$	2,4	1,2	a,b
$I\bar{4}$	MZX	$P\bar{4}(\tau_1,\tau_2)$	2,2,4	1,1,2	a,a,b
	A	$I\bar{4}(\tau_1,\tau_2)$	4	2	c
	N	$I\bar{4}(\tau_1)$	8	4	f_4
P4/m	Z	$P4/m(\tau_1,\tau_5)$, $P4_2/m(\tau_2,\tau_6)$	2	1	a
	M	$P4/m(\tau_1,\tau_2)$, $P4/n(\tau_5,\tau_6)$			
	A	$I4/m(\tau_1,\tau_2,\tau_5,\tau_6)$			
	R	$I4/m(\tau_1 \to \tau_4)$	4	2	b
	X	$P4/m(\tau_1,\tau_4)$, $P4/n(\tau_2,\tau_3)$			
$P4_2/m$	M	$P4_2/m(\tau_1,\tau_2)$, $P4_2/n(\tau_5,\tau_6)$	2	1	a
	R	$I4_1/a(\tau_1 \to \tau_4)$	4	2	b
	X	$P4_2/m(\tau_1,\tau_4)$, $P4_2/n(\tau_2,\tau_3)$			
P4/n	Z	$P4/n(\tau_1,\tau_5)$, $P4_2/n(\tau_2,\tau_6)$	2	1	a
$P4_2/n$	A	$I4_1/a(\tau_1,\tau_2,\tau_5,\tau_6)$			
I4/m	MZ	$P4/m(\tau_1)$, $P4_2/m(\tau_2)$ $P4/n(\tau_5)$, $P4_2/n(\tau_6)$			
	X	$P4/m(\tau_1)$, $P4_2/n(\tau_2)$ $P4/n(\tau_3)$, $P4_2/m(\tau_4)$	4	2	b
	A	$(I4/m,I4_1/a)(\tau_1,\tau_2)$			
	N	$I4/m(\tau_1)$, $I4_1/a(\tau_2)$	8	4	f_4
P422	Z	$P422(\tau_1,\tau_2)$,$P4_222(\tau_3,\tau_4)$	2	1	a
	MX	$P422(\tau_1,\tau_3)$,$P42_12(\tau_2,\tau_4)$	2,4	1,2	a,b
	AR	$I422(\tau_1 \to \tau_4)$			
$P42_12$	Z	$P42_12(\tau_1,\tau_2)$, $P4_22_12(\tau_3,\tau_4)$	2	1	a
$P4_122$	MX	$P4_122(\tau_1,\tau_3)$, $P4_12_12(\tau_2,\tau_4)$	2,4	1,2	a,b
$P4_222$	Z	$P4_122(\tau_2,\tau_5)$, $P4_322(\tau_3,\tau_4)$	2	1	a
	MX	$P4_222(\tau_1,\tau_3)$, $P4_22_12(\tau_2,\tau_4)$	2,4	1,2	a,b
	A	$I4_122(\tau_2 \to \tau_5)$	2	1	a
	R	$I4_122(\tau_1 \to \tau_4)$	4	2	b
$P4_22_12$	Z	$P4_12_12(\tau_2,\tau_5)$, $P4_32_12(\tau_3,\tau_4)$	2	1	a
$P4_322$	MX	$P4_322(\tau_1,\tau_3)$, $P4_32_12(\tau_2,\tau_4)$	2,4	1,2	a,b
I422	MZ	$P422(\tau_1)$, $P42_12(\tau_2)$, $P4_222(\tau_3)$, $P4_22_12(\tau_4)$	2	1	a
	X	$P422(\tau_1)$, $P4_22_12(\tau_2)$, $P4_222(\tau_3)$, $P42_12(\tau_4)$	4	2	b
	A	$(I422,\ I4_122)(\tau_1,\tau_4)$			
	N	$I422(\tau_1,\tau_2)$	8	4	f_4
$I4_122$	MZ	$P4_12_12(\tau_2)$, $P4_322(\tau_3)$, $P4_32_12(\tau_4)$, $P4_122(\tau_5)$	2	1	a
	X	$P4_12_12(\tau_1)$, $P4_322(\tau_2)$, $P4_122(\tau_3)$, $P4_32_12(\tau_4)$	4	2	b
P4mm	Z	$P4mm(\tau_1)$, $P4cc(\tau_2)$, $P4_2mc(\tau_3)$, $P4_2cm(\tau_4)$	2	1	a
	M	$P4mm(\tau_1,\tau_3)$, $P4bm(\tau_2,\tau_4)$			
	A	$I4mm(\tau_1,\tau_3)$, $I4cm(\tau_2,\tau_4)$			
	X	$P4mm(\tau_1,\tau_2)$, $P4bm(\tau_3,\tau_4)$	4	2	b
	R	$I4mm(\tau_1,\tau_2)$, $I4cm(\tau_3,\tau_4)$			
P4bm	Z	$P4bm(\tau_1)$, $P4nc(\tau_2)$, $P4_2bc(\tau_3)$, $P4_2nm(\tau_4)$	2	1	a
$P4_2cm$	M	$P4_2mc(\tau_1,\tau_3)$, $P4_2bc(\tau_2,\tau_4)$			
	X	$P4_2cm(\tau_1,\tau_2)$, $P4_2nm(\tau_3,\tau_4)$	4	2	b
$P4_2nm$	A	$I4_1md(\tau_1,\tau_3)$, $I4_1cd(\tau_2,\tau_4)$	2	1	a
P4cc	M	$P4cc(\tau_1,\tau_3)$, $P4nc(\tau_2,\tau_4)$			
	X	$P4cc(\tau_1,\tau_2)$, $P4nc(\tau_3,\tau_4)$	4	2	b
$P4_2mc$	M	$P4_2cm(\tau_1,\tau_3)$, $P4_2nm(\tau_2,\tau_4)$	2	1	a
	X	$P4_2mc(\tau_1,\tau_2)$, $P4_2bc(\tau_3,\tau_4)$	4	2	b
	R	$I4_1md(\tau_1,\tau_3)$, $I4_1cd(\tau_2,\tau_4)$			
I4mm	MZ	$P4mm(\tau_1)$,$P4nc(\tau_2)$,$P4_2mc(\tau_3)$,$P4_2nm(\tau_4)$	2	1	a
	X	$P4mm(\tau_1)$, $P4_2cm(\tau_2)$, $P4bm(\tau_3)$, $P4_2nm(\tau_4)$	4	2	b
	A	$(I4mm,I4_1md)(\tau_1)$,$(I4cm,I4_1cd)(\tau_3)$			
	N	$I4mm(\tau_1)$, $I4cm(\tau_2)$	8	4	f_4
I4cm	MZ	$P4bm(\tau_1)$,$P4cc(\tau_2)$,$P4_2bc(\tau_3)$,$P4_2cm(\tau_4)$	2	1	a
	X	$P4nc(\tau_1)$,$P4_2mc(\tau_2)$,$P4cc(\tau_3)$,$P4_2bc(\tau_4)$	4	2	b

TABLE III (*Continued*).

(a)	(b)	(c)	(d)	(e)	(f)
$P\bar{4}2m$	Z	$P\bar{4}2m(\tau_1,\tau_4)$, $P\bar{4}2c(\tau_2,\tau_3)$	2	1	a
	M	$P\bar{4}m2(\tau_1,\tau_3)$, $P\bar{4}b2(\tau_2,\tau_4)$			
	A	$I\bar{4}m2(\tau_1,\tau_4)$, $I\bar{4}c2(\tau_2,\tau_3)$			
	X	$P\bar{4}2m(\tau_1,\tau_3)$, $P\bar{4}2_1m(\tau_2,\tau_4)$	4	2	b
	R	$I\bar{4}2m(\tau_1 \rightarrow \tau_4)$			
$P\bar{4}2c$	M	$P\bar{4}c2(\tau_1,\tau_3)$, $P\bar{4}n2(\tau_2,\tau_4)$	2	1	a
	X	$P\bar{4}2m(\tau_1,\tau_3)$, $P\bar{4}2_1m(\tau_2,\tau_4)$	4	2	b
	R	$I\bar{4}2d(\tau_1 \rightarrow \tau_4)$			
$P\bar{4}2_1m$	Z	$P\bar{4}2_1m(\tau_1,\tau_3)$, $P\bar{4}2_1c(\tau_2,\tau_4)$	2	1	a
$P\bar{4}m2$	Z	$P\bar{4}m2(\tau_1,\tau_4)$, $P\bar{4}c2(\tau_2,\tau_3)$			
	M	$P\bar{4}2m(\tau_1,\tau_4)$, $P\bar{4}2_1m(\tau_2,\tau_3)$			
	A	$I\bar{4}2m(\tau_1 \rightarrow \tau_4)$			
	X	$P\bar{4}m2(\tau_1,\tau_2)$, $P\bar{4}b2(\tau_3,\tau_4)$	4	2	b
	R	$I\bar{4}m2(\tau_1,\tau_3)$, $I\bar{4}c2(\tau_2,\tau_4)$			
$P\bar{4}c2$	M	$P\bar{4}2c(\tau_1,\tau_4)$, $P\bar{4}2_1c(\tau_2,\tau_3)$	2	1	a
	X	$P\bar{4}c2(\tau_1,\tau_2)$, $P\bar{4}n2(\tau_3,\tau_4)$	4	2	b
$P\bar{4}b2$	Z	$P\bar{4}b2(\tau_1,\tau_4)$, $P\bar{4}n2(\tau_2,\tau_3)$	2	1	a
$P\bar{4}n2$	A	$I\bar{4}2d(\tau_1 \rightarrow \tau_4)$			
$I\bar{4}m2$	M,Z	$P\bar{4}m2(\tau_1,\tau_4)$, $P\bar{4}n2(\tau_2,\tau_3)$			
	X	$P\bar{4}m2(\tau_1,\tau_2)$, $P\bar{4}n2(\tau_3,\tau_4)$	4	2	b
	N	$I\bar{4}m2(\tau_1)$, $I\bar{4}c2(\tau_2)$	8	4	f_4
	A	$(I\bar{4}2m, I\bar{4}2d)(\tau_1,\tau_2)$	4	2	b
$I\bar{4}c2$	M,Z	$P\bar{4}c2(\tau_1,\tau_4)$, $P\bar{4}b2(\tau_2,\tau_3)$	2	1	a
	X	$P\bar{4}2c(\tau_1,\tau_2)$, $P\bar{4}2_1c(\tau_3,\tau_4)$	4	2	b
$I\bar{4}2m$	MZ	$P\bar{4}2m(\tau_1)$, $P\bar{4}2_1c(\tau_2)$ $P\bar{4}2c(\tau_3)$, $P\bar{4}2_1m(\tau_4)$	2	1	a
	X	$P\bar{4}m2(\tau_1)$, $P\bar{4}c2(\tau_2)$ $P\bar{4}b2(\tau_3)$, $P\bar{4}n2(\tau_4)$	4	2	b
	N	$I\bar{4}2m(\tau_1)$, $I\bar{4}2d(\tau_2)$	8	4	f_4
	A	$I\bar{4}m2(\tau_1,\tau_4)$, $I\bar{4}c2(\tau_2,\tau_3)$	4	2	c
$P4/mmm$	Z	$P4/mmm(\tau_1,\tau_7)$, $P4/mcc(\tau_2,\tau_6)$, $P4_2/mmc(\tau_3,\tau_9)$, $P4_2/mcm(\tau_4,\tau_8)$	2	1	a
	M	$P4/mmm(\tau_1,\tau_3)$, $P4/mbm(\tau_2,\tau_4)$, $P4/nbm(\tau_6,\tau_8)$, $P4/nmm(\tau_7,\tau_9)$			
	A	$I4/mmm(\tau_1,\tau_3,\tau_7,\tau_9)$, $I4/mcm(\tau_2,\tau_4,\tau_6,\tau_8)$			
	X	$P4/mmm(\tau_1,\tau_7)$, $P4/nmm(\tau_2,\tau_8)$, $P4/nbm(\tau_3,\tau_5)$, $P4/mbm(\tau_4,\tau_6)$	4	2	b
	R	$I4/mmm(\tau_1,\tau_3,\tau_7,\tau_8)$, $I4/mcm(\tau_2,\tau_4,\tau_5,\tau_6)$			
$P4/mcc$	M	$P4/mcc(\tau_1,\tau_3)$, $P4/mnc(\tau_2,\tau_4)$, $P4/nnc(\tau_6,\tau_8)$, $P4/ncc(\tau_7,\tau_9)$	2	1	a
	X	$P4/mcc(\tau_1,\tau_3)$, $P4/ncc(\tau_7,\tau_9)$, $P4/nnc(\tau_3,\tau_5)$, $P4/mnc(\tau_4,\tau_6)$	4	2	b
$P4/nbm$	Z	$P4/nbm(\tau_1,\tau_7)$, $P4/nnc(\tau_2,\tau_6)$, $P4_2/nbc(\tau_3,\tau_9)P4_2/nnm(\tau_4,\tau_8)$	2	1	a
$P4/mbm$	Z	$P4/mbm(\tau_1,\tau_7)$, $P4/mnc(\tau_2,\tau_6)$, $P4_2/mbc(\tau_3,\tau_9)$, $P4_2/mnm(\tau_4,\tau_8)$			
$P4/nmm$	Z	$P4/nmm(\tau_1,\tau_7)$, $P4/ncc(\tau_2,\tau_6)$, $P4_2/nmc(\tau_3,\tau_9)$, $P4_2/ncm(\tau_4,\tau_8)$			
$P4_2/mmc$	M	$P4_2/mcm(\tau_1,\tau_3)$, $P4_2/nnm(\tau_7,\tau_9)$, $P4_2/mnm(\tau_2,\tau_4)$, $P4_2/ncm(\tau_6,\tau_8)$			
	X	$P4_2/mcm(\tau_1,\tau_7)$, $P4_2/nmc(\tau_2,\tau_8)$, $P4_2/nbc(\tau_3,\tau_5)$, $P4_2/mbc(\tau_4,\tau_6)$	4	2	b
	R	$I4_1/amd(\tau_1,\tau_3,\tau_7,\tau_8)$, $I4_1/acd(\tau_2,\tau_4,\tau_5,\tau_6)$			
$P4_2/mcm$	M	$P4_2/mmc(\tau_1,\tau_3)$, $P4_2/nbc(\tau_6,\tau_8)$, $P4_2/mbc(\tau_2,\tau_4)$, $P4_2/nmc(\tau_7,\tau_9)$	2	1	a
	X	$P4_2/mcm(\tau_1,\tau_7)$, $P4_2/ncm(\tau_2,\tau_8)$, $P4_2/nnm(\tau_3,\tau_5)$, $P4_2/mnm(\tau_4,\tau_6)$	4	2	b
$P4_2/nnm$	A	$I4_1/amd(\tau_1,\tau_2,\tau_6,\tau_7)$, $I4_1/acd(\tau_3,\tau_4,\tau_8,\tau_9)$	2	1	a
$I4/mmm$	MZ	$P4/mmm(\tau_1)$, $P4/mnc(\tau_2)$, $P4_2/mmc(\tau_3)$, $P4_2/mnm(\tau_4)$ $P4/nnc(\tau_6)$, $P4/nmm(\tau_7)$, $P4_2/nnm(\tau_8)$, $P4_2/nmc(\tau_9)$			
	X	$P4/mmm(\tau_1)$, $P4/nbm(\tau_5)$, $P4/mbm(\tau_4)$, $P4/nmm(\tau_8)$ $P4_2/mcm(\tau_6)$, $P4_2/nnm(\tau_2)$, $P4_2/mnm(\tau_7)$, $P4_2/ncm(\tau_3)$	4	2	b
	N	$I4/mmm(\tau_1,\tau_4)$, $I4/mcm(\tau_2,\tau_3)$	8	4	f_4
	A	$I4/mmm(\tau_1,\tau_3,\tau_4)$, $I4/mcm(\tau_2,\tau_3,\tau_4)$ $I4_1/amd(\tau_1,\tau_2,\tau_4)$, $I4_1/acd(\tau_3)$	4	2	b
$I4/mcm$	MZ	$P4/mcc(\tau_1)$, $P4/mbm(\tau_2)$, $P4_2/mcm(\tau_3)$, $P4_2/mbc(\tau_4)$ $P4/nbm(\tau_6)$, $P4/ncc(\tau_7)$, $P4_2/nbc(\tau_8)$, $P4_2/ncm(\tau_9)$	2	1	a
	X	$P4/mcc(\tau_1)$, $P4/nnc(\tau_5)$, $P4/mnc(\tau_4)$, $P4/ncc(\tau_8)$ $P4_2/mmc(\tau_6)$, $P4_2/nbc(\tau_2)$, $P4_2/mbc(\tau_7)$, $P4_2/nmc(\tau_3)$	4	2	b

marginal importance to the checking of the Lifschitz condition[15] as this condition is necessarily obeyed[12] by an IR having an "active" star k^*, and whose small representation is real and one dimensional. We only have to examine, in this respect, the IR's for which τ_n is complex. This is the case for only six *BZ* points, having the property that $\vec{k} \neq (-\vec{k})$: *R* (orthorhombic lattice *I*), *A* (tetragonal *I*), *K* and *H* (hexagonal), *W* (cubic *F*), and *P* (cubic *I*).[17] By contrast, the one dimensionality of τ_n does not simplify the checking of the Landau criterion.[12] As shown by our investigation, this criterion even appears as a very selective condition for the IR's of the rhombohedral, hexagonal, and cubic systems. Thus, among the τ_n examined, nearly one half is discarded by the Landau condition. As these IR's are as liable as the "active" ones to describe the transitions of real systems, we can expect that a significant fraction of the observed NFPT's, within a rhombohedral, hexagonal, or cubic crystal class, will display a first-order transition due to the fact that their order-parameter expansion contains a term of degree-three.

The established property provides a necessary condition for an IR to preserve the point symmetry of the crystal. This condition is not sufficient in general. It has, however, been shown to be sufficient[12] in the case where τ_n is real and when $k^* \neq 0$ has one arm. In this case the IR itself is real and one dimen-

TABLE IV. NFPT's in the rhombohedral and the hexagonal systems.

(a)	(b)	(c)	(d)	(e)	(f)
$P3$	AHL	$P3(\tau_1)$	2,6,8	1,2,3	a,d,e
$P3_1$		$P3_2(\tau_1)$			
$P3_2$		$P3_1(\tau_1)$			
$R3$	ZA	$R3(\tau_1)$	2,8	1,3	a,e
$P\bar{3}$	A	$P\bar{3}(\tau_1,\tau_4)$	2	1	a
	HL	$P\bar{3}(\tau_1)$	6,8	2,3	d,e
$R\bar{3}$	Z	$R\bar{3}(\tau_1,\tau_4)$	2	1	a
	A	$R\bar{3}(\tau_1,\tau_2)$	8	3	e
$P312$	A	$P312(\tau_1,\tau_4)$	2	1	a
	L	$P312(\tau_1)$	8	3	e
	H	$P321(\tau_1)$	6	2	d
$P321$	A	$P321(\tau_1,\tau_2)$	2	1	a
	L	$P321(\tau_1)$	8	3	e
	H	$P312(\tau_1,\tau_2)$	6	2	d
$P3_112$	A	$P3_212(\tau_3)$	2	1	a
	L	$P3_212(\tau_1)$	8	3	e
	H	$P3_221(\tau_1)$	6	2	d
$P3_121$	A	$P3_221(\tau_2,\tau_3)$	2	1	a
	L	$P3_221(\tau_1)$	8	3	e
	H	$P3_212(\tau_2,\tau_3)$	6	2	d
$P3_212$	A	$P3_112(\tau_2,\tau_3)$	2	1	a
	L	$P3_212(\tau_1)$	8	3	e
	H	$P3_121(\tau_1)$	6	2	d
$P3_221$	A	$P3_121(\tau_2,\tau_3)$	2	1	a
	L	$P3_121(\tau_1)$	8	3	e
	H	$P3_112(\tau_2,\tau_3)$	6	2	d
$R32$	ZA	$R32(\tau_1,\tau_2)$	2,8	1,3	a,e
	X	$R32(\tau_2)$	4	3	e
$P3m1$	AL	$P3m1(\tau_1)$, $P3c1(\tau_2)$	2,8	1,3	a,e
	H	$(P31m, P31c)(\tau_1)$	6	2	d
$P31m$	AL	$P31m(\tau_1)$, $P31c(\tau_2)$	2,8	1,3	a,e
	H	$P3m1(\tau_1)$, $P3c1(\tau_2)$	6	2	d
$R3m$	ZA	$R3m(\tau_1)$, $R3c(\tau_2)$	2,8	1,3	a,e
	X	$R3m(\tau_2)$	4	3	e
$R3c$	X	$R3c(\tau_2)$	4	3	e
$P\bar{3}1m$	A	$P\bar{3}1m(\tau_1,\tau_4)$, $P\bar{3}1c(\tau_2,\tau_5)$	2	1	a
	L	$P\bar{3}1m(\tau_1,\tau_4)$, $P\bar{3}1c(\tau_2,\tau_3)$	8	3	e
$P\bar{3}m1$	A	$P\bar{3}m1(\tau_1,\tau_4)$, $P\bar{3}c1(\tau_2,\tau_5)$	2	1	a
	L	$P\bar{3}m1(\tau_1,\tau_4)$, $P\bar{3}c1(\tau_2,\tau_3)$	8	3	e
$R\bar{3}m$	Z	$R\bar{3}m(\tau_1,\tau_4)$, $R\bar{3}c(\tau_2,\tau_5)$	2	1	a
	A	$R\bar{3}m(\tau_1,\tau_3)$, $R\bar{3}c(\tau_2,\tau_4)$	8	3	e
	X	$R\bar{3}m(\tau_2,\tau_3,\tau_4)$	4		
$R\bar{3}c$	X	$R\bar{3}c(\tau_2,\tau_3,\tau_4)$			
$P6$	AL	$P6(\tau_1)$, $P6_3(\tau_2)$	2,8	1,3	a,e
	H	$(P6,P6_3)(\tau_1)$	6	2	d
$P6_2$	A	$P6(\tau_1)$, $P6_4(\tau_2)$	2	1	a
	L	$P6_4(\tau_1)$, $P6_1(\tau_2)$	6	3	e
	H	$(P6_1,P6_4)(\tau_1)$	6	2	d
$P6_4$	AL	$P6_2(\tau_1)$, $P6_5(\tau_2)$	2,8	1,3	a,e
	H	$(P6_2,P6_5)(\tau_1)$	6	2	d
$P\bar{6}$	AH	$P\bar{6}(\tau_1,\tau_4)$	2,6	1,2	a,d
	L	$P\bar{6}(\tau_1,\tau_2)$	8	3	e
$P6/m$	A	$P6/m(\tau_1,\tau_7)$, $P6_3/m(\tau_2,\tau_8)$	2	1	a
	L	$P6/m(\tau_1,\tau_3)$, $P6_3/m(\tau_2,\tau_4)$	8	3	e
	H	$(P6/m,P6_3/m)(\tau_1,\tau_4)$	6	2	d
$P622$	A	$P622(\tau_1,\tau_2)$, $P6_322(\tau_3,\tau_4)$	2	1	a
	L	$P622(\tau_1,\tau_4)$, $P6_322(\tau_2,\tau_3)$	8	3	e
	H	$(P622,P6_322)(\tau_1,\tau_2)$	6	2	d
$P6_222$	A	$P6_422(\tau_2,\tau_3)$, $P6_122(\tau_5,\tau_6)$	2	1	a
	L	$P6_122(\tau_2,\tau_3)$, $P6_422(\tau_1,\tau_4)$	8	3	e
	H	$(P6_122,P6_422)(\tau_1,\tau_2)$	6	2	d
$P6_422$	A	$P6_222(\tau_2,\tau_3)$, $P6_522(\tau_5,\tau_6)$	2	1	a
	L	$P6_222(\tau_1,\tau_4)$, $P6_522(\tau_2,\tau_3)$	8	3	e
	H	$(P6_222,P6_522)(\tau_1,\tau_2)$	6	2	d
$P6mm$	A	$P6mm(\tau_1)$, $P6cc(\tau_2)$ $P6_3mc(\tau_3)$, $P6_3cm(\tau_4)$	2	1	a
	L	$P6mm(\tau_1)$, $P6cc(\tau_3)$ $P6_3cm(\tau_2)$, $P6_3mc(\tau_4)$	8	3	e
	H	$(P6mm,P6_3cm)(\tau_1)$ $(P6cc,P6_3mc)(\tau_2)$	6	2	d
$P\bar{6}m2$	A	$P\bar{6}m2(\tau_1,\tau_5)$, $P\bar{6}c2(\tau_2,\tau_4)$	2	1	a
	L	$P\bar{6}m2(\tau_1,\tau_4)$, $P\bar{6}c2(\tau_2,\tau_3)$	8	3	e
	H	$(P\bar{6}2m,P\bar{6}2c)(\tau_1,\tau_4)$	6	2	d
$P\bar{6}2m$	A	$P\bar{6}2m(\tau_1,\tau_5)$, $P\bar{6}2c(\tau_2,\tau_4)$	2	1	a
	L	$P\bar{6}2m(\tau_1,\tau_4)$, $P\bar{6}2c(\tau_2,\tau_3)$	8	3	e
	H	$P\bar{6}m2(\tau_1,\tau_5)$, $P\bar{6}c2(\tau_2,\tau_4)$	6	2	d
$P6/mmm$	A	$P6/mmm(\tau_1,\tau_8)$, $P6/mcc(\tau_2,\tau_7)$ $P6_3/mmc(\tau_3,\tau_{10})$, $P6_3/mcm(\tau_4,\tau_9)$	2	1	a
	L	$P6/mmm(\tau_1,\tau_8)$, $P6/mcc(\tau_4,\tau_5)$ $P6_3/mcm(\tau_2,\tau_6)$, $P6_3/mmc(\tau_3,\tau_7)$	8	3	e
	H	$(P6/mmm,P6_3/mcm)(\tau_1,\tau_5)$ $(P6/mcc,P6_3/mmc)(\tau_2,\tau_4)$	6	2	d

sional. It will systematically induce a NFPT corresponding to a subgroup of index 2,[11] i.e., to a doubling of the unit cell. In the other cases, for stars having several arms, or for complex τ_n, the possible occurrence of a NFPT has to be examined in detail for each IR.

We can also notice in Eq. (3) that, because of the independence on $\vec{k}$ of the C_n coefficients, all the arms of the star k^* are simultaneously "frozen in" in the low-symmetry phase. This has the consequence that a NFPT always involves[12,15] the maximum loss of translational symmetry compatible with the corresponding order parameter.

We have summarized in Tables I to V the crystallographical and physical results relative to the order-parameter symmetries and space-group changes relative to all possible continuous NFPT's. The tables have been ordered according to the crystal system common to the two phases: triclinic and monoclinic (Table I), orthorhombic (Table II), tetragonal (Table III), rhombohedral-hexagonal (Table IV), and cubic (Table V). Similarly to the tables published previously for other types of transitions, the present ones allow the determination of the following characteristics of each NFPT: (i) space-symmetry change and unit-cell multiplication, (ii) identification, dimension, and symmetry properties of the transition's order parameter (OP), and (iii) form of the OP expansion

TABLE V. NFPT's in the cubic system.

(a)	(b)	(c)	(d)	(e)	(f)	(g)
$P23$	R	$F23(\tau_1)$	2	1	a	C_i
	X	$P23(\tau_1,\tau_2),P2_13(\tau_3,\tau_4)$	8	3	e	T_h
$F23$	L	$F23(\tau_1)$	8	4	f_3	95.1
$I23$	P	$F23(\tau_1)$	4	2	c	C_4
	H	$P23(\tau_1)$	2	1	a	C_i
$I2_13$	H	$P2_13(\tau_1)$	2	1	a	C_i
$Pm3$	R	$Fm3(\tau_1,\tau_5)$	2	1	a	C_i
	X	$Pm3(\tau_1,\tau_6),Pn3(\tau_2,\tau_5)$ $Pa3(\tau_3,\tau_4,\tau_7,\tau_8)$	8	3	e	T_h
$Pn3$	R	$Fd3(\tau_1,\tau_5)$	2	1	a	C_i
$Fm3$	L	$Fm3(\tau_1)$, $Fd3(\tau_4)$	8	4	f_3	95.1
$Im3$	P	$(Fm3,Fd3)(\tau_1)$	4	2	b	C_{4v}
	H	$Pm3(\tau_1),Pn3(\tau_5)$	2	1	a	C_i
$Ia3$	H	$Pa3(\tau_1,\tau_5)$	2	1	a	C_i
$P432$	R	$F432(\tau_1,\tau_2)$	2	1	a	C_i
	X	$P432(\tau_1,\tau_3),P4_232(\tau_2,\tau_4)$	8	3	e	O_H
$P4_232$	R	$F4_132(\tau_1,\tau_2)$	2	1	a	C_i
	X	$P4_232(\tau_2,\tau_3),P4_132(\tau_4,\tau_5)$	8	3	e	O_H
$F432$	L	$F432(\tau_1),F4_132(\tau_2)$	8	4	f_3	109.01
	W	$P432,P4_232$ $P4_132,P4_332$ (τ_1,τ_4)	32	6	h_1	L_2
$I432$	P	$(F432,F4_132)(\tau_1)$	4	2	b	C_{4v}
	H	$P432(\tau_1),P4_232(\tau_2)$	2	1	a	C_i
$I4_132$	H	$P4_332(\tau_1),P4_132(\tau_2)$	2	1	a	C_i
$P\bar{4}3m$	R	$F\bar{4}3m(\tau_1),F\bar{4}3c(\tau_2)$	2	1	a	C_i
	X	$P\bar{4}3m(\tau_1),P\bar{4}3n(\tau_2)$	8	3	e	O_H
$F\bar{4}3m$	L	$F\bar{4}3m(\tau_1),F\bar{4}3c(\tau_2)$	8	4	f_3	109.01
	W	$(P\bar{4}3m,P\bar{4}3n)(\tau_1,\tau_2)$	32	6	h_1	L_3
$I\bar{4}3m$	P	$F\bar{4}3m(\tau_1),F\bar{4}3c(\tau_2)$	4	2	c	C_4
	H	$P\bar{4}3m(\tau_1),P\bar{4}3n(\tau_2)$	2	1	a	C_i
$Pm3m$	R	$Fm3m(\tau_1,\tau_6),Fm3c(\tau_2,\tau_7)$	2	1	a	C_i
	X	$Pm3m(\tau_1,\tau_3),Pm3n(\tau_2,\tau_4)$ $Pn3n(\tau_6,\tau_8),Pn3m(\tau_7,\tau_9)$	8	3	e	O_H
$Pn3m$	R	$Fd3m(\tau_1,\tau_6)Fd3c(\tau_2,\tau_7)$	2	1	a	C_i
$Fm3m$	L	$Fm3m(\tau_1),Fm3c(\tau_2)$ $Fd3m(\tau_4),Fd3c(\tau_5)$	8	4	f_3	109.01
	W	$(Pm3m,Pm3n)(\tau_1,\tau_4)$ $(Pn3n,Pn3m)(\tau_2,\tau_3)$	32	6	h_1	L_1
$Im3m$	P	$(Fm3m,Fd3m)(\tau_1)$ $(Fm3c,Fd3c)(\tau_2)$	4	2	b	C_{4v}
	H	$Pm3m(\tau_1),Pm3n(\tau_2)$ $Pn3n(\tau_6),Pn3m(\tau_7)$	2	1	a	C_i

TABLE VI. Materials undergoing a nonferroic phase transition.

Substances	T_c (°C) or P_c (kbar)or x (at.comp)	Order	Space-group change	Unit-cell expansion	Brillouin zone point	Order Parameter dimension	Table number	References
$C_sH_3(SeO_3)_2$	- 128	1	$P\bar{1} \to P\bar{1}$	2	$Z(\tau_1,\tau_2)$	1	I	19
$Ag_2H_3IO_6$	- 45	2			$B(\tau_1,\tau_2)$			25
$Na_{1-x}K_xNbO_3$	x ∿ 0.33	-	Pm → Pm	2	$B(\tau_2)$	1	I	30
N.N. Dymethylnitramine	- 166	2	$P2_1/m \to P2_1/b$		$Y(\tau_2,\tau_3)$			7
$Bi_2Ti_4O_{11}$	250	2	B2/m → B2/b		$(B,Y,C)(\tau_2,\tau_3)$			31
$C_6Cl_4O_2$	- 181	2	$P2_1/b \to P2_1/b$		$A(\tau_1 \to \tau_4)$			5
$C_{10}H_7Cl$	35	-						26
$Cu(HCOO)_2.4H_2O$	- 39	1						29
$C_{10}F_8$	- 7	1						6
Bis-P.Toluene sulfonate di cetylene	- 78	2						28
$(C_{20}H_{18}O_6S_2)_n$	- 103	2						27
$CsFeF_4$	150	2	Pmma → Pmmn	2	$Y(\tau_4,\tau_3)$	1	II	38
C_sVF_4	-	1						39
K Fe F_4	95 290	2 1	Cmcm → Pmmn Cmmm → Cmcm		$Y(\tau_7)$ $Z(\tau_2,\tau_3,\tau_6,\tau_7)$			40
K V F_4	255	2	Cmcm → Pmmn		$Y(\tau_7)$			
K Ti F_4	215	1						
$(C_2H_5NH_3)_2MnCl_4$	- 48	1	Cmca → Pbca		$Y(\tau_3)$			34
$(C_2H_5NH_3)_2CdCl_4$	- 57	1						
$(C_3H_7NH_3)_2MnCl_4$	- 93	1	Cmca → Pbam		$Y(\tau_1)$			35
$(C_3H_7NH_3)_2CdCl_4$	-	-						
$(C_{10}H_{21}NH_3)_2CdCl_4$	39	1	Cccm → Pnnm		$Y(\tau_4)$			36
$NH_3(CH_2)_3NH_3MnCl_4$	32	2	Imma → Pnma		$X(\tau_3,\tau_7)$			33,37
$NH_3(CH_2)_3NH_3CdCl_4$	103	2						
$NH_3(CH_2)_5NH_3CdCl_4$	68	2						
KCN	- 190	1	Immm → Pmmn		$X(\tau_6,\tau_7,\tau_8)$			8
NaCN	- 101	1						
$C_{18}H_{24}$	30	-	Immm → Fddd	4	$R(\tau_1 \to \tau_4)$	2		41
$CH_3NH_3CdCl_4$	6	1	$I4/mmm \to P4_2/ncm$	4	$X(\tau_3)$	2	III	32
$CH_3NH_3MnCl_4$	- 16	1						
$(NH_4)_2H_3IO_6$	- 21	1	R3 → R3	2	$Z(\tau_1)$	1	IV	25
$PbZr_xTi_{1-x}O_3$	x = 0.63	-	R3m → R3c	2	$Z(\tau_1)$	1		
$PbZr_{0.9}Ti_{0.1}O_3$	100	1		8	$A(\tau_2)$	3		42
$NaNO_3$	275	2	$R\bar{3}m \to R\bar{3}c$	2	$Z(\tau_2,\tau_5)$	1		44
$YMnO_3$	1 000	(1)	$P6_3/mmc \to P6_3/mcm$	3	$K(\tau_1)$	2	Ref. 47	46
Mg_3Cd	150	1	$P6_3/mmc \to P6_3/mmc$	4	$M(\ _1)$	3		48
Ti_3Al	1 150	1						
EuO	∿ 400 kbar	1	Fm3m → Pm3m	4	$X(\tau_1)$	3	Ref.47	50
EuTe	∿ 110 kbar	1						
EuS	∿ 215 kbar	1						
EuSe	∿ 145 kbar	1						
SmTe	∿ 110 kbar	1						
PrTe	∿ 90 kbar	1						
Cu_3AuI	394	1						49
α"Au_3CuI	200	1						
$Fe_{1-x}Al_x$	x ∿ 0.50 x ∿ 0.26	1 2	Im3m → Fm3m	4	$P(\tau_1)$	2	V	
Fe_3Al	550	2						
Fe_3Si	1 130	-						
β-Cu_2MnAl	630	-						
β-CuZn	425	2	Im3m → Pm3m	2	$H(\tau_1)$	1		
$Ag_{2-x}Au_xS$	x ∿ 0.29	2						

TABLE VII. Different types of order-parameter expansions associated to the NFPT's. (a) Labeling of the expansions as in Ref. 14. (b) Expression as a function of the order-parameter components. (c) Brillouin-zone points and crystalline systems associated with each type of expansion. (d) Image (see Ref. 14) of the order-parameter representation giving rise to the expansion. (e) Number of unequivalent low-symmetry phases. (f) and (g) Absolute minima and corresponding range of the expansion's coefficients.

(a)	(b)	(c)	(d)	(e)	(f)	(g)
a	$\frac{\alpha}{2}\eta^2+\frac{\beta}{4}\eta^4$	all	Ci	1	$\eta\neq 0$	$\beta>0$
b	$\frac{\alpha}{2}(\eta^2+\zeta^2)+\left\{\frac{\beta_1}{4}(\eta^4+\zeta^4)+\frac{\beta_2}{2}\eta^2\zeta^2\right.$	MoB,orth(C,I),Tet,P (Cub I)	C_{4v}	2	$\eta=\zeta\neq 0$ $\eta\neq 0,\quad =0$	$\beta_1>\beta_2$ $\beta_1<\beta_2$ $\beta_1>0$
c	$\frac{\beta_1}{4}(\eta^4+\zeta^4)+\frac{\beta_2}{2}\eta^2\zeta^2+\beta_3\eta\zeta(\eta^2-\zeta^2)$	R (orth I),A(Tet I) ,P(Cub I)	C_4	1	$\eta\neq\zeta\neq 0$	$\beta_1>0$
d	$\frac{\alpha}{2}\rho^2+\frac{\beta_1}{4}\rho^4+\frac{\gamma_1}{6}\rho^6+\left\{\frac{\gamma_2}{6}\rho^6\cos 6\varphi\right.$	H (Hex)	C_{6v}	2	$\rho\neq 0,\varphi=0$ $\rho\neq 0,\varphi=\frac{\pi}{2}$	$\beta_1>0,\ \gamma_2<0$ $\beta_1>0,\ \gamma_2>0$
	$\frac{\gamma_2}{6}\rho^6\cos 6\varphi+\frac{\gamma_3}{6}\rho^6\sin 6\varphi$		C_6	1	$\rho\neq 0,\ \mathrm{tg}\ 6\varphi=\frac{\gamma_3}{\gamma_2}$	$\beta_1>0,\ \gamma_2\cos 6\varphi<0$
e	$\frac{\alpha}{2}\sum\limits_{i=1,3}\eta_i^2+\frac{\beta_1}{4}\sum\limits_{i=1,3}\eta_i^4+\frac{\beta_2}{2}\sum\limits_{i<j=1,3}\eta_i^2\eta_j^2$	A(Rh), L(Hex), X(Cub P)	T_h,O_h	1	$\eta_1=\eta_2=\eta_3\neq 0$	$\beta_1>0,\ \beta_1>\beta_2>-\beta_1$
f_3	$\frac{\alpha}{2}\sum\limits_{i=1,4}\eta_i^2+\left\{\frac{\beta_1}{4}I_o+\frac{\beta_2}{2}(I_1+I_2+I_3)+\beta_3 I_4\right.$	L (cub F)	95.1,109.01	2	$\eta_1=\eta_2=\eta_3=\varepsilon\eta_4\neq 0\ (\varepsilon=\pm 1)$	$2\beta_1>\varepsilon\beta_3,\beta_1+3\beta_2+\varepsilon\beta_3>0$ $2\beta_1-\varepsilon\beta_3>\lvert 2\beta_2+\varepsilon\beta_3\rvert$ $2\beta_1+4\beta_2+\varepsilon\beta_3>0$
f_4	$\frac{\beta_1}{4}I_o+\frac{\beta_2}{2}I_1+\frac{\beta_3}{2}I_2+\frac{\beta_4}{2}I_3$	N (Tet I)	58.01,82.01	1	$\eta_1=\eta_2=\eta_3=\eta_4\neq 0$	$\beta_1>0,\ \beta_1>\lvert\beta_2\rvert$ $\beta_1(\beta_1^2-\beta_2^2-\beta_3^2-\beta_4^2)+2\beta_2\beta_3\beta_4>0$ $\sum\limits_{i=1,4}\beta_i^4-2\sum\limits_{i<j}\beta_i^2\beta_j^2+8\beta_1\beta_2\beta_3\beta_4>0$
f_5	$\frac{\beta_1}{4}I_o+\frac{\beta_2}{2}I_1+\frac{\beta_3}{2}I_2+\frac{\beta_4}{2}I_3+\beta_5 I_4$	R (orth F)	56.1	2	$\eta_1=\eta_2=\eta_3=\varepsilon\eta_4\neq 0\ (\varepsilon=\pm 1)$	$a_i=2\beta_i+\varepsilon\beta_5(i=1,4),\ a_1>0,\ a_1>\lvert a_2\rvert$ $a_1^3-a_1(a_2^2+a_3^2+a_4^2)+2\varepsilon a_2a_3a_4>0$ $\sum\limits_{i=1,4}a_i^4-2\sum\limits_{i<j}a_i^2a_j^2+8\varepsilon a_1a_2a_3a_4>0$
h_1	$\frac{\alpha}{2}\sum\limits_{i=1,3}\rho_i^2+\frac{\beta_1}{4}\sum\limits_{i=1,3}\rho_i^4+\frac{\beta_2}{4}\rho_i^4\cos 4\varphi_i+$ $+\frac{\beta_3}{2}\sum\limits_{i<j}\rho_i^2\rho_j^2+\frac{\gamma_1}{6}\sum\limits_{i=1,3}\rho_i^6+\frac{\gamma_2}{6}\sum\limits_{i=1,3}\rho_i^6\cos 4\varphi_i+$ $+\frac{\gamma_3}{4}\sum\limits_{i\neq j}\rho_i^4\rho_j^2+\frac{\gamma_4}{4}\sum\limits_{i\neq j}\rho_i^4\rho_j^2\cos 4\varphi_i+$ $+\frac{\gamma_5}{2}\rho_1^2\rho_2^2\rho_3^2+\frac{\gamma_6}{2}\rho_1^2\rho_2^2\rho_3^2\cos 2\varphi_1\cos 2\varphi_2\cos 2\varphi_3$	W(Cub F) Fm3m	L_1	2	$\rho_1=\rho_2=\rho_3\neq 0$ $\varphi_i=0\ (i=1,3)$	$\gamma_6<0$ $\beta_3<0$ $\beta_1-\lvert\beta_3\rvert>\beta_2$ $\beta_2>\frac{\beta_1-\lvert\beta_3\rvert}{2}$
		$F\bar{4}3m$	L_3		$\rho_1=\rho_2=\rho_3\neq 0$ $\varphi_i=\frac{\pi}{2}\ (i=1,3)$	$\gamma_6>0$
		F432	L_2	4	$\rho_1=\rho_2=\rho_3\neq 0$, $\varepsilon=-1$, $\varphi_i=o$	$\gamma_6<0$ $\beta_3\varepsilon<0$ $\beta_1-\lvert\beta_3\rvert>\varepsilon_2$ $\beta_2>-\frac{\beta_1-\lvert\beta_3\rvert}{2}$
					$\varphi_i=\frac{\pi}{2}$	$\gamma_6>0$
					$\rho_1=\rho_2=\rho_3\neq 0$, $\varepsilon=+1$, $\varphi_i=\frac{\pi}{4}$	$\gamma_6<0$
					$\varphi_i=\frac{3\pi}{4}$	$\gamma_6>0$

$I_o=\sum\limits_{i=1,4}\eta_i^4$; $I_1=\eta_1^2\eta_2^2+\eta_3^2\eta_4^2$; $I_2=\eta_1^2\eta_3^2+\eta_2^2\eta_4^2$; $I_3=\eta_1^2\eta_4^2+\eta_2^2\eta_3^2$; $I_4=\eta_1\eta_2\eta_3\eta_4$; $\rho^2=\eta^2+\zeta^2$, $\eta=\rho\cos\varphi$, $\zeta=\rho\sin\varphi$; $\rho_i^2=\eta_i^2+\zeta_i^2$, $\eta_i=\rho_i\cos\varphi_i$, $\zeta_i=\rho_i\sin\varphi_i$ $(i=1,3)$

$F_1(n_i)$ with the range of values of each of the expansion coefficients corresponding to the stabilities of the different phases.

The tables are organized in the same way as in Refs. 12–14. The content of the columns is recalled in the Appendix. Some general results can be drawn from examination of the tables.

In the first place, it appears that on theoretical grounds, NFPT's should be a very frequent type of structural transitions: among the 3000 IR of the space groups which are related to continuous crystalline transitions, over 1200 determine a symmetry change towards a nonferroic phase. The only other type of structural transition which arises, in the framework of Landau's theory, with a comparable frequency, is that of pure ferroelastics.[14]

In general, the symmetry characteristics of NFPT's are very simple due to the one dimensionnality of the small representation τ_n. Thus in about two-thirds of the possible transitions, the order parameter is one dimensional, and the translational change consists in a doubling of the crystal's unit cell. This situation is the one encountered with few exceptions in the triclinic, monoclinic, and orthorhombic systems and it also constitutes the major pattern in the quadratic one. It is also found for one $\vec{k}$ vector of the rhombohedral hexagonal systems and for two $\vec{k}$ vectors of the cubic one.

The remaining cases can be grouped in three types. In the triclinic, monoclinic, orthorhombic, and tetragonal systems the transitions have either a two-dimensional or a four-dimensional OP and are accompanied, respectively, by a fourfold and an eightfold multiplication of the unit cell. In the trigonal-hexagonal systems two specific patterns are found: a three-dimensional OP determining an eightfold unit-cell expansion, and a two-dimensional OP associated to a sixfold multiplication. The cubic system combines the various preceding cases with, in addition, transitions associated to a six-dimensional OP. In particular, one finds the latter dimensionality at the W point of the BZ of the face-centered cubic lattice. At this point the NFPT determines a 32-fold multiplication of the primitive unit cell. This steep decrease of translational symmetry was well known[11] to be the largest possible in a continuous structural transition. The present study clarifies the fact that such a multiplication is necessarily associated to a NFPT, while any other type of structural transition would involve a smaller multiplication of the unit cell.

According to the definition of a NFPT, the transitions considered take place between two space groups belonging to the same crystal class. Following the terminology of Hermann,[18] the low-symmetry group is a "klassengleichen" subgroup of the high-symmetry group, i.e., a subgroup having the same point group but different translations. In this respect, a number of crystallographical studies have been devoted to the generation of the "klassengleischen" subgroups of the space groups.[19–23] Following extensive works by Neubüser *et al.*[19] and Koptsik,[23] summarizing tables have been established by Boyle and Lawrenson (BL).[20] A comparison of the present results to those of BL, besides providing a useful checking, permits clarification of the additional restrictions imposed by the Landau theory on a purely geometrical relationship between crystallographic groups.

As pointed out by BL, klassengleichen subgroups of a given space group form an infinite set if any unit-cell multiplication is allowed. Accordingly, BL have limited this multiplication to a factor, depending of the crystal system dealt with. For instance, this factor is 32 in the orthorhombic system. Comparison to the results in Tables III–VII shows that the physical restrictions of Landau's theory (mainly based on Lifschitz's criterion) are much narrower. The nonferroic groups worked out here constitute a small fraction of the groups found in the tables of BL. Thus, in the $P222$ space group, we find a doubling of the unit cell towards any of the nonferroic groups while BL indicate unit-cell multiplications by factors of 2, 4, 8, 16, and 32.

On the other hand, it is worth comparing our results to those of Syromiatnikov[24] also based on geometrical rules, in which the same selection of $\vec{k}$ vectors as in Landau's theory is taken into account, but no use is made of the irreducible representations or of the thermodynamical considerations. As we pointed out previously,[14] the method of Syromiatnikov supplies the same symmetry changes as Landau's theory only when the small representation is one dimensional. This explains why we have been able to verify a frequent identity of the present results to those of Syromiatnikov tables. Two differences can be noted. In the first place, nonferroic symmetry changes, which are absent from our tables due to their incompatibility with the Landau and Lifschitz criteria for continuous transitions, appear in Syromiatnikov's work indistinctly mixed to the "continuous" symmetry changes. On the other hand, a given symmetry change is indicated only once, in their table, for each star of $\vec{k}$ vectors, while such a change can happen to be associated to various order-parameter symmetries having a common star.

III. NONFERROIC MATERIALS

About 50 substances have been listed in Table VI. They constitute illustrative examples of nonferroic symmetry changes. They belong to a wide diversity of chemical compositions: metallic alloys, salts, hydrates, molecular solids, and oxides. The phase transitions considered are either induced by a temperature change, by a pressure change, or by a compositional change. Let us compare these data to the theoretical results of Sec. II.

A. Triclinic and monoclinic systems

In these systems all available examples fit into the pattern expected to be most frequent for NFPT's. They are found to possess a one-dimensional order parameter and a double unit cell below the transition. We have been able to check the compliance of the observed symmetry changes with the results of Table I, and to identify, on this basis, their order parameter.

Two compounds undergo the triclinic modification $P\bar{1} \rightarrow P\bar{1}$ with a doubling of the primitive unit cell, CsH_3 $(SeO_3)_2$ (Ref. 19) and $Ag_2H_3IO_6$. For the latter material there is a sequence of transitions, one of which has been conjectured to be a NFPT in the framework of a theoretical interpretation.[25]

In the monoclinic system most available examples display a uniform symmetry scheme, i.e., the space-group change $P2_1/b \rightarrow P2_1/b$ with a doubling of the microscopic periodicity along either the a or the b direction. This scheme is mainly realized in organic compounds such as chloranil,[5] chloronaphthlene,[26] octafluoronaphthalene,[6] the polysulfonyl $(C_{20}H_{18}O_6S_2)_n$,[27] the diacetylpolymer[28] bis (*p*-toluene sulfonate) and copper formate tetrahydrate.[29] Their order parameter can be identified by one of the four IR's at the A point $(k = a^*/2)$ of the Brillouin zone (Table I).

Similar monoclinic NFPT's are observed in NN-dimethylnitramine[7] $(P2_1/m \rightarrow P2_1/b)$ with a doubling along $\vec{c}$, and in $Na_{1-x}K_xNbO_3$. In the latter material, which has a distorted perovskite structure, and displays a number of stable phases according to the external conditions, the considered NFPT occurs between the phases labeled L, and K,[30] on decreasing the potassium content below $x = 0.33$. These two phases have cells, respectively, four and eight times larger than the cubic perovskite cell.

In $Bi_2Ti_4O_{11}$, the space-group change is known $(B2/m \rightarrow B2/b)$ but the available data[31] are insufficient to specify the translational symmetry of the order parameter. Tables I and VI show that three BZ points, namely, B, Y, and C are compatible with the observed unit-cell doubling transition.

B. Orthorhombic and quadratic systems

Two families with layered structures and displaying NFPT's, have been recently the subjects of intensive studies.

The first one is the perovskite layers structural family. It contains several categories of compounds differing by their chemical formulas and the sequence of the layers forming their structures.

In the so-called ammonium series of general formula $(C_nH_{2n+1}NH_3)_2\,MCl_4$, four types of NFPT take place. In the methyl compounds $(n = 1)$ with $M = (Cd,Mn)$, the tetragonal space-group change $I4/mmm \rightarrow P4_2/ncm$ occurs, through an orthorhombic intermediate phase.[32] Table III shows, in agreement with a previous theoretical analysis,[33] that the order parameter is two dimensional and described by the τ_3 representation at the X point[17] of the body-centered tetragonal BZ. In the ethyl $(n = 2)$ and propyl $(n = 3)$ compounds a NFPT takes place for $M = (Cd, Mn)$ with, respectively, the symmetry changes $Cmca \rightarrow Pbca$,[34] and $Cmca \rightarrow Pbam$,[35] likewise the compound $n = 10$, $M = Cd$ undergoes the change $Cccm \rightarrow Pnnm$.[36] All these NFPT's have a one dimensional OP corresponding to the Y point of the BZ (Table II).

In the less-studied diammonium series of formula $NH_3(CH_2)_nNH_3MCl_4$, NFPT's have been reported[33,37] for $n = 3$ $(M = Mn,\ Cd)$ and $n = 5$ $(M = Cd)$ with the space-group change $Imma \rightarrow Pnma$. Table II shows that two representations at the X point of the BZ can possibly induce this transition.

The second structural family of interest has the formula ABF_4 $(A = Rb,\ Cs,\ K$ and $B = Fe,\ V,\ Ti)$. Two distinct sequences of transitions exist in it. The first one has been observed complete[38] in $CsFeF_4$ and partial[39] in $CsVF_4$ and $RbFeF_4$. It is

$$P4/mmm(\vec{t}_1, \vec{t}_2, \vec{t}_3) \rightarrow Pmma(\vec{t}_1, 2\vec{t}_2, \vec{t}_3) \rightarrow Pmmn(2\vec{t}_1, 2\vec{t}_2, \vec{t}_3) \rightarrow P2_12_12(2\vec{t}_1, 2\vec{t}_2, \vec{t}_3) \ .$$

The NFPT *Pmma-Pmmn* occurs continuously in $CsFeF_4$ and discontinuously in $CsVF_4$. It is induced by a one-dimensional IR as disclosed by Table II.

The second sequence characterizes the compounds[40] KMF_4. It consists in the symmetry changes

$$Ammm(v) \rightarrow Amma(2v) \rightarrow Pmmn(4v) \ .$$

The first NFPT occurs in KF_eF_4 at 290 °C and appears related to the Z point (Table II) of the Brillouin zone. The other one, *Amma-Pmmn* is observed as a continuous transition in $KFeF_4$ and KVF_4 and as a discontinuous one in KT_iF_4. The theoretical results associate its order parameter to the IR labeled τ_4 at the Y point of the *BZ*.

Besides these two structural families three examples of orthorhombic NFPT's have been listed on Table VI. The cyanides KCN and NaCN possess, in addition to a ferroelastic transition, a low-temperature NFPT detected, respectively, at -190 and -101 °C. The corresponding symmetry change $Immm \rightarrow Pmmm$ involves a doubling of the ferroelastic cell which can be related to one of the three IR's (τ_6, τ_7, or τ_8) of the orthorhombic X point (I lattice). At last, let us mention the NFPT observed in the organic compound[41] triamantane $C_{18}H_{24}$. Its ordered phase is described by the space group $Fddd$ and possess a unit cell four times larger than the body-centered prototypic phase of symmetry $Immm$. According to Table II, a two-component OP corresponding to one of the four IR's at the R point should be associated with this transition.

C. Rhomboedral and hexagonal systems

Three compounds are known to possess a rhomboedral NFPT. In the solid solutions $PbZr_xTi_{1-x}O_3$ a transition occurs with increasing x at $x=0.63$. The space-group change is $R3m \rightarrow R3c$ corresponding to the BZ corner point ($\vec{k}=\frac{1}{2},\frac{1}{2},\frac{1}{2}$) precedingly pointed out by Cochran and Zia[42] (Table IV). In $PbZr_{0.9}Ti_{0.1}O_3$ another type of NFPT takes place at 100 °C or by varying the temperature. This polar-polar transition, which is slightly first order,[43] is described by the same space-group change $R3m \rightarrow R3c$ but with an octupling of the primitive cell corresponding to the A point ($\vec{k}=\frac{1}{2},0,0$) of the rhomboedral BZ. Sodium nitrate undergoes[44] at 275 °C, a continuous transition $R\overline{3} \rightarrow R\overline{3}c$, just below its melting point. Petzelt *et al.*[45] assign to it, in accordance with the results in Table IV a one-dimensional IR at the Z point of the Brillouin zone. Ammonium periodate, $(NH_4)_3H_3IO_6$, like its silver isomorph, displays a more intricate situation.[25] Two-phases transitions have been detected in it by thermal analysis measurements. Only the extreme phases have been identified as $R\overline{3}$ and $R3$, with an eightfold expansion of the unit cell. Roos *et al.*[25] suggested that the lowest transition is an isomorphous transition $R3$-$R3$ without translational change. An alternate scheme can be based on the results of Table IV and of Ref. 12. It involves the sequence of a ferroelectric transition[12] $R\overline{3}\ (v) \rightarrow R3\ (4v)$ having a three-component order parameter, and a NFPT, $R3\ (4v) \rightarrow R3\ (8v)$, with a double periodicity along the ternary axis. The latter symmetry change is absent from Table IV as it does not comply with the Landau condition.

A hexagonal NFPT has been observed in $YMnO_3$ at about 1000 °C.[46] The space-group change $P6_3/mmc \rightarrow P6_3/mcm$ involves the unusual tripling of unit cell determined by an inactive[47] IR at the K point[18] of the BZ. Other inactive IR's are involved in the hexagonal NFPT of a number of alloys, such as Mg_3Cd and Ti_3Al possessing the AB_3 type[10,48] of structure. The corresponding space-group change is $P6_3/mmc\ (v) \rightarrow P6_3/mmc\ (4v)$ and is related to the M point[17] of the BZ. The transitions are of first order consistently with the inactive character of their order parameter. The same symmetry change has been observed in Mg_3Cd, Al_3Th, Pt_3U, CO_3Mo, CO_3W, and βNi_3Sn.[49]

D. Cubic system

Members of the rare-earth monochalcogenides family and a large number of substances belonging to various alloys systems can be given as examples of cubic nonferroic materials. A widespread characteristic of NFPT's in this crystal system are their noncompliance with the Landau symmetry criterion. This is, in particular, the case of rare-earth monochalcogenides. This family is best known for the occurrence of a pressure-induced semiconductor-metal transition involving a change of valence of the rare-earth ion. In addition to this change, high-pressure studies have revealed[50] a pressure-induced structural change from the NaCl structure $Fm3m$ to the CsCl one ($Pm3m$) in the two compounds SmTe and EuO.

In other compounds, namely, PrTe, EuS, EuSe, and EuTe, only the structural change NaCl→CsCl is observed with no electronic modification. This change which involves a fourfold-larger cell is actually a NFPT induced by a three-dimensional inactive IR[47] at the X point of the cubic (F) BZ. A strongly discontinuous volume change at the transition confirms its first-order character, in agreement with the noncompliance of the preceeding representation with the Landau condition.

All the cubic alloys listed on Table VI possess a phase transition within the $m3m$ class. These transitions correspond, on a phenomenological basis, to three distinct situations. One is the type of transformation taking place in the archetypical β-brass (CuZn) and in several isomorphous compounds such as Au-Cd, Al-Ni, Ni-Zn, or LiTl.[10,49] The corresponding space-group change $Im3m\ (v) \rightarrow Pm3m\ (2v)$ is induced by the unidimensional IR(τ_1) of the H point[17] of the cubic body-centered BZ. A very similar situation is encountered in $Ag_{2-x}Au_xS$ (Ref. 51) which undergoes a compositional transition at $x \sim 0.29$ with the space-group change associated to another representation (τ_4) of the same H point.

A second type of transition is found in the Fe-Al system and in the so-called Heusler alloys isostructural to Cu_2MnAl. In the Fe-Al system a temperature-dependent transformation ($Im3m \rightarrow Fm3m$) can take place continuously at 550 °C in alloys containing about 26 at.% Al. The same symmetry change occurs dependent on the composition in $Fe_{1-x}Al_x$ when x reaches 25 at.%. According to Table V it is a bidimensional OP at the P point [cubic (I) BZ], which is associated to the $Im3m \rightarrow Fm3m$ change involving a quadrupling of the primitive cell.

The preceding space-group modification corresponds also to the $L2_1$ type[10,49] of superlattice appearing in the metastable β phase of Cu_2MnAl, and in many ternary alloys such as Cu_2MSn (M = Co, Mn, Fe, Ni), Ni_2TiAl, $LiMg_2Tl$, or CO_2MnSn. Other similar transitions are found in α'-Fe_3Si, β_1-AlCu, H_3La, AIF_3, $HgLi_3$, $LaMg_3$, β-Cu_3Sb, and Mg_3Pr.

A third type of NFPT within the $m3m$ class is the transformation which occurs in Cu_3AuI from the high-temperature disordered state ($Fm3m$) to the order state ($Pm3m$) at 394 °C. This structural change is also detected in a large number of alloys the more studied of which are α''-Au_3CuI, Ni_3Fe, Ni_3Mn, Pt_3Sn, and α'-$AlCO_3$.[49] The discontinuous character of the 394 °C transition in Cu_3AuI is in agreement with the fact that the corresponding three-dimensional OP transforms like the τ_1 IR of the X point (cubic F BZ) which does not comply with the Landau criterion.[47] The same IR induces the composition-dependent transition observed in $Fe_{1-x}Al_x$ when x reaches 50% of Al atoms, the Fe-Al structure being then of the $B2$ type.

We have not included in Table VI the fluorite compound $PbSnF_4$ as its nonferroic character still requires experimental confirmations. However, it deserves to be quoted as it is the single known example of a NFPT involving a multiplication by 32 of the number of atoms in the primitive unit cell, this situation being predicted in Table V at the W point of the $F432$, $F43m$, and $Fm3m$ space groups. Structural data are given by Pannetier and co-workers[52–54] for three phases, labeled γ, β, and α with decreasing temperature, separated by two transitions occurring, respectively, at 370–380 and 260–290 °C. The γ phase has a fluorite-type structure (space group $Fm3m$) with $a = 6.050$ Å and β-$PbSnF_4$ has a tetragonal unit cell (unspecified space group) with $a = 16.834$ Å and $c = 23.063$ Å, i.e., with a unit-cell dimension 128 times larger than the cubic F one. When using the results of Tables III and V and of Ref. 14 it appears that, within Landau's theory predictions, there is only one sequence of three transitions capable to produce the lattice modifications reported for the $\gamma \rightarrow \beta$ change, the higher-temperature one being the NFPT $Fm3m(v) \rightarrow Fm3m\,(32v)$.

These transitions have not yet been clearly detected but they could explain the complex thermal expansion of the lattice parameters between 280 and 380 °C mentioned by Pannetier *et al.*[54] The $Fm3m \rightarrow Fm3m$ transition should thus be related to the endothermic effect measured around 350 °C by these authors and to the $\beta' \rightarrow \beta$ transition reported at 350 °C in Refs. 53 and 54.

IV. PHENOMENOLOGICAL THEORY OF NONFERROIC TRANSITIONS

Let us examine, in this section, the characteristics of the Landau free energy of a NFPT and the consequences of its form on the behavior of macroscopic quantities. In this respect, no distinction has to be made, as would be the case for ferroics, between a proper and an improper behavior.[14] These concepts corresponded to a classification based on the respective symmetries of the order parameter and of the symmetry-breaking macroscopic components. No such components onset below a NFPT. Nevertheless, it is relevant to take into account, in the free energy which describes a NFPT, in addition to the order parameter expansion $F_1(\eta_i)$, terms relative to the macroscopic quantities which couple to the order parameter.

As noticed previously by various authors,[14,55] the order-parameter expansions $F_1(\eta_i)$ relative to continuous transitions, possess a small number of possible forms. This situation, which contrasts with the large variety of space-group representations considered, results from two simplifications. In the first place, the form of the free energy only depends on the set of distinct matrices relative to the IR spanned by the order parameter. It was shown in Ref. 14 that only 49 sets were associated to the thousands of "active" IR's of the 230 crystallographic space groups. On the other hand, the truncation of the expansion to the 4th degree further reduces the number of distinct expansions to 27. Nine of these expansions are relevant to the order parameters of NFPT's. They are reproduced in Table VII together with the conditions of stability they determine for the various low-symmetry phases.

The coupling of a macroscopic quantity (x_j) with the order parameter (η_i) is represented in the free-energy expansion by terms of the form $\phi(\eta_i)\cdot\psi(x_j)$, where ϕ and ψ have identical symmetries, and where $\phi(\eta_i) \neq 0$ in the low-symmetry phase (terms with $\phi(\eta_i) = 0$ can be omitted for the considered transition). For a NFPT, the point group is the same for both phases and $\psi(x_j)$ necessarily transforms according to the identical representation of Go. Any other symmetry would induce a breakdown of the point symmetry through the onset of a spontaneous value for $\psi(x_j)$. Consequently $\phi(\eta_i)$ is also totally invariant, and we have, to lowest degree (δ is a coefficient):

$$\phi(\eta_i)\psi(x_j) = \delta\left[\sum_i \eta_i^2\right]\psi(x_j) \quad . \tag{10}$$

On Table VIII, we have expressed the set of ψ_k functions having the smallest degree, in the two cases when the x_j are the polarization components P_j ($j = 1,2,3$) and the strain ones e_{ij} ($i,j = 1,2,3$). It can be seen that only two different qualitative situa-

TABLE VIII. Lowest-degree invariants X_i and Y_i of the polarization components and of the strain ones which can be coupled to the order-parameter invariant $(\sum \eta_i^2)$. The invariants are listed in column (b) according to their distribution in the 32 crystal classes [column (a)]. The expression of the X_i and the Y_i is indicated in column (c), respectively, as a function of the polarization components P_x, P_y, P_z, and of the strain ones $e_{ij}(i,j=1,2,3)$ referred to standard axes. The δ_i and δ_{ij} are the coefficients of the resulting coupling terms.

(a)	(b)	(c)
1	X_1, Y_1	$X_1=\delta_1 P_x+\delta_2 P_y+\delta_3 P_z$
$\bar{1}$	x_2, Y_1	$X_2=\delta_1 P_x^2+\delta_2 P_y^2+\delta_3 P_z^2$
2	X_3, Y_3	$X_3=\delta_1 P_x^2+\delta_2 P_y^2+\delta_3 P_z$
m	X_4, Y_3	$X_4=\delta_1 P_x+\delta_2 P_y+\delta_3 P_z^2$
$2/m$	X_2, Y_3	$X_5=\delta_1(P_x^2+P_y^2)+\delta_2 P_z$
$mm2$	X_3, Y_2	$X_6=\delta_1(P_x^2+P_y^2)+\delta_2 P_z^2$
$222, mmm$	X_2, Y_2	$X_7=\delta_1(P_x^2+P_y^2+P_z^2)$
$4, 4mm$	X_5, Y_4	$Y_1=\sum_{i,j}\delta_{ij}e_{ij}$
$\bar{4}, 4/m, 422, \bar{4}m2, 4/mmm$	X_6, Y_4	$Y_2=\sum_i \delta_{ii}e_{ii}+\sum_{i\neq j}\delta_{ij}e_{ij}^2$
$3, 3m, 6, 6mm$	X_5, Y_5	$Y_3=\sum_i \delta_{ii}e_{ii}+\delta_{12}e_{12}+\delta_{13}e_{13}^2+\delta_{23}e_{23}^2$
$\bar{3}, 32, \bar{3}m, \bar{6}, 6/M$	X_6, Y_5	$Y_4=\delta_1 e_{33}+\delta_1'(e_{11}+e_{22})+\delta_2(e_{13}^2+e_{23}^2)+\delta_3 e_{12}^2+\delta_4(e_{11}-e_{22})^2$
$622, \bar{6}m2, 6/mmm$		$Y_5=\delta_1 e_{33}+\delta_1'(e_{11}+e_{22})+\delta_2[(e_{11}-e_{22})^2+4e_{12}^2]+\delta_3(e_{13}^2+e_{23}^2)$
$23, m3, \bar{4}3m, 432, m3m$	X_7, Y_6	$Y_6=\delta_1(e_{13}^2+e_{23}^2+e_{12}^2)+\delta_2[3(e_{11}-e_{22})^2+2(e_{33}-e_{11}-e_{22})^2]$

tions are encountered together or separately for NFPT's: one corresponds to a linear contribution of the P_j or e_{ij} to the coupling term, a second one to a quadratic contribution. It is obvious that the first situation for the P_j's occurs in the ten pyroelectric classes 1, 2, *m*, *mm*2, 4, 4*mm*, 3, 3*m*, 6, 6*mm*. A linear coupling with some of the e_{ij} components is possible in all the crystalline systems. The strain contribution to the mixed invariant being the same within a given system.

Due to the totally symmetric form $(\sum \eta_i^2)$ of the order-parameter contribution to the coupling term, no qualitative difference will exist in the macroscopic anomalies between the case of a one component order parameter and that of a multicomponent one. We can therefore restrict to the former simpler situation and examine for instance the coupling to the dielectric polarization. The discussion for elastic quantities would be similar. The two possible coupling schemes will give rise to the two following free energies:

$$F_A(\eta,P)=\frac{\alpha}{2}\eta^2+\frac{\beta}{4}\eta^4+\frac{\gamma}{6}\eta^6+\frac{K}{2}P^2+\frac{\delta}{2}\eta^2P^2-EP\ , \tag{11}$$

$$F_B(\eta,P)=\frac{\alpha}{2}\eta^2+\frac{\beta}{4}\eta^4+\frac{\gamma}{6}\eta^6+\frac{K}{2}P^2+\delta\eta^2P-EP+\lambda P\ . \tag{12}$$

The electric field component E parallel to P has been introduced to derive the dielectric susceptibility $\chi=\lim_{E\to Q}(P/E)$ and the electric dependence of the polarization $P(E)$. As usually in the Landau phenomenological description all the coefficients except α are taken constant in the neighborhood of the transition point as their temperature dependence is not determined by the existence of a phase transition. α which depends linearly on the temperature, can be written $\alpha = a(T - T_0)$ $(a > 0)$ and thus changes of sign at T_0. The coefficient K has to be chosen as positive, λ must be taken as negative if we take the orientation of the crystal towards $P > 0$. The sign of the δ coefficient has to be discussed in relation with the different physical situations encountered.

The physical consequences of expansion F_A have been examined in detail by Levanyuk *et al.*,[56] while expansion F_B, which is formally similar to the free energy of an improper ferroelectric, has been discussed by several authors.[57,58]

The free energy F_A induces no permanent polarization component on either side of the transition.[59] The behavior of the dielectric susceptibility has a temperature dependence determined by $\chi = (1/K + \delta\eta^2)$. It is illustrated by Fig. 1 according to the sign of δ and the thermodynamic order of the transition. As emphasized by Levanyuk *et al.*, whenever the transition is discontinuous, a double hysteresis loop $P(E)$ should appear above or below T_c depending on the sign of δ.

The dielectric behavior resulting from the free energy F_B is summarized on Fig. 2. Identically to the case of an improper ferroelectric, the susceptibility is temperature independent above the transition and undergoes an upward jump at T_c whatever the sign of δ and the order of the transition. A "spontaneous" additional component of P onsets in the low-symmetry phase, but no multiple orientations exist for it and accordingly no orientational domains are induced. For a first-order transition, a double hysteresis loop in $P(E)$ is predicted above T_c.

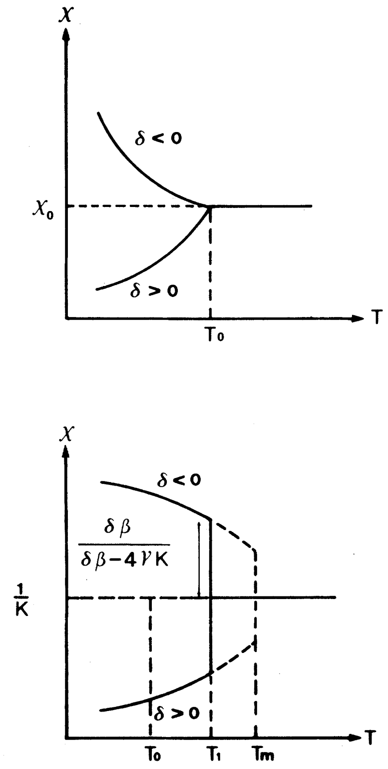

FIG. 1. Variations of the dielectric susceptibility for a NFPT the order parameter of which is coupled to the polarization through a term of the form $\eta^2 P^2$. The notations are those of Eq. (11). Upper diagram: second-order transition. Lower diagram: first-order transition.

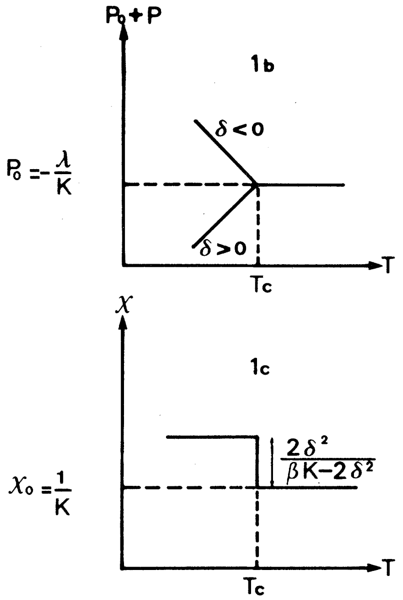

FIG. 2. Schematic variations of the polarization P, and of the dielectric susceptiblity χ for a continuous NFPT the order parameter of which is coupled to the polarization through a term of the form $P\eta^2$. The notations are those of Eq. (12).

For a small number of the nonferroic materials listed on Table VI, dielectric studies have been performed which permit, incompletely still, to check the preceding phenomenological predictions. Only two of these materials possess a polar-polar phase transition described by the F_B free energy, namely, $PbZr_xTi_{1-x}O_3$ and $(NH_4)_2H_3IO_6$. The others correspond to the F_A type.

The nonferroic transition in the perovskite $PbZr_xTi_{1-x}O_3$ occurs around 100 °C for $x = 0.90$ and provokes a slope variation in the spontaneous polarization P_s. Below the transition point the polarization increases linearly with decreasing temperature suggesting a continuous character as shown in Fig. 2(b) $(\delta < 0)$. However, by providing the slight discontinuity of the OP (the rhomboedral angle α), the transition should be weakly first order as indicated by Clarke and Glazer.[43] The two-step transition in amonium orthoperiodate has been recently reinvestigated by Roos *et al.*[25] who have confirmed the early measurement of Baerthschi[60] of a two-step decreasing of the dielectric permitivity ϵ_c in the direction of the polar axis. The lower step is in conformity with the curve of Fig. 2(d) ($\delta < 0$). There is an obvious resemblance between the theoretical curve of Fig. 1(a) ($\delta > 0$) and the experimental variation of $\chi(T)$ obtained for $Bi_2Ti_4O_{11}$ by Subbarao.[61] Besides it has been verified by this author that no hysteresis loop exists in either phase of these compounds. Both these facts are consistent with a second-order character for the nonferroic monoclinic transition at 250 °C.

The orthorhombic −190 °C transition in potassium cyanide has been reported as second order.[62] However, the anomaly of the dielectric permittivity at this temperature measured by Gesi[63] displays a typical first-order drop as the one shown in Fig. 1(b) ($\delta > 0$). The discontinuity of the permittivity at −190 °C is even accentuated in the study by Julian and Luty,[64] the slight increase of $\epsilon(T)$ in the high-symmetry phase on the experimental curve should be due to the influence of the neighboring ferroelastic transition at −105 °C.[63]

Two other nonferroics, which should also illustrate the F_A-type behavior, reveal a more complex situation. In **cesium trihydrogen selenite** $CsH_3(SeO_3)_2$ a study by Makita[9] shows that the dielectric constant along the [001] direction has the behavior depicted in Fig. 4 ($\delta > 0$) in agreement with the first-order character reported for its −128 °C triclinic transition.[9] But, on the other hand, the dielectric constant perpendicular to the (001) plane exhibits a pronounced peak at the transition point with a sharp decrease in both phases, in contradiction with the constant value of $\chi(T)$ predicted on Fig. 4. The same situation is verified for copper formate tetrahydrate $Cu(HCOO)_2 4H_2O$ at its monoclinic transition at −39 °C. The dielectric constant in the (100) plate has a small drop resembling Fig. 4 ($\delta > 0$), but in the (010) plate Okada[29] finds an acute discontinuity with a decrease on either sides of the transition point.

The peculiar increase of the susceptibility in the high-symmetry phase of the two preceding substances has been accounted for by their antiferroelectric character, i.e., by the presence in their structures of pairs of opposed dipoles onsetting below T_c. This presence has been established by a variety of experimental techniques.[25,43]

It was recognized by Levanyuk *et al.*[56] that there is an equivalence between the free energy F_A and the one worked out by Kittel[65] for antiferroelectric transitions, provided that the K coefficient in Eq. (11) is allowed to increase (e.g., linearly) with temperature. On this basis it is possible to account for the observed behavior of the preceding substances. Thus, the anisotropy of the dielectric permittivity of both $CsH_3(SeO_3)_2$ and $Cu(HCOO)_2 \cdot 4H_2O$ can be explained, on one hand by the different magnitudes of the coupling coefficient δ_i, and on the other hand by the fact that only part of the components of $K(T)$, which is a second-rank tensor in the three-dimensional case, are temperature dependent. As an illustration, for cesium selenite, which is triclinic and possesses a one-component OP, the coupling term must be written (see Table I) $(\delta_1 P_x^2 + \delta_2 P_y^2 + \delta_3 P_z^2)\eta^2$, but as it appears from Makita's experimental results[9], one must take here $\delta_3 \ll \delta_2 \simeq \delta_1/2$.

From the formal identity of Kittel's theory of antiferroelectrics and Eq. (11), Levanyuk *et al.*[56] have concluded that the characteristics of antiferroelectrics actually belong to a larger class of substances than those possessing arrays of opposite dipoles. They have also noted that the division of an electric dipole distribution is ambiguous and that the concept of an antiferroelectric is, in fact, irrelevant. This remark clearly holds for ionic crystals. However for molecular ones like Copper formate tetrahydrate or in crystals having covalent units like potassium cyanide, assignment of individual dipoles to these structural units appears justified. For these cases, the association of antiferroelectricity with the preservation of the crystal class seems puzzling since the onset of sets of opposite dipoles in a crystal's unit cell has generally been thought to give rise to ferroelastic properties. This inference was based on the fact that the lowest multipolar moment generated by a pair of opposite dipoles is a quadrupole, i.e., a tensorial quantity of the same rank as the ferroelastic spontaneous strain.[14] Ferroelastic symmetry changes have indeed been observed in a number of antiferroelectrics, such as $NaNbO_3$, $(NH_4)HPO_4$, etc. More complex arrays of dipoles, for instance two pairs of opposite dipoles, can correspond to the onset of a higher-rank multipole. In this case, the symmetry characteristics of the antiferroelectric transition will be that of a "**secondary ferroic**."[13]

The preservation of the crystal class by the onset of opposite dipoles can be understood by examining the case of KCN. In this crystal, the dipoles are situated at the vertices and at the center of a body centered orthorhombic lattice with symmetry *Immm*. The ones at the vertices are parallel to the *b* direction while the one at the center is antiparallel to it. The resulting space symmetry is *Pmmm* corresponding to the same *mmm* class as the underlying lattice. The array of dipoles does generate a nonzero quadrupole. However the spontaneous component of this second-rank tensor is the Q_{22} component which is already permitted by symmetry in the high-temperature phase and it does not break the point symmetry of the crystal.

This example, and that of the other antiferroelectric NFPT's clarifies the symmetry aspect of antiferroelectricity. In the most frequent case where a single set of opposite dipoles arises in the unit cell, two situations can be found. Either the component of the generated quadrupole are symmetry-breaking ones and the corresponding transition will be ferroelastic, or these components preserve the orientational symmetry and one obtains a NFPT.

V. CONCLUSION

The group-theoretical investigation of NFPT has disclosed several peculiarities of these categories of transitions. Most possible transitions, on theoretical grounds, are expected to have a one-component order parameter and to induce a doubling of unit cell. This property is closely related to the theorem which has been established for the class-preserving transitions and which discards all the multidimensional small representations of the group of the $\vec{k}$ vector. At experimental level the observed NFPT in real systems comply well with the preceding theoretical expectation.

On the other hand, the working out of the Landau and Lifschitz symmetry criteria has shown that in the rhombohedral, hexagonal, and cubic systems, a large fraction of the relevant order parameters will give rise to a cubic term in the Landau free-energy expansion and induce a first-order transition. A number of illustrative examples of this situation have been found among metallic alloys.

The characteristics of the dielectric anomalies at NFPT's have been satisfactorily accounted for on the basis of two possible schemes for the coupling between the order parameter and the dielectric polarization. In some cases previously classified among antiferroelectrics, the phenomenological theory has to be refined in the form of a temperature dependence for two coefficients instead of one as in the usual theory.

APPENDIX: ORGANIZATION OF TABLES I TO V

Let us briefly describe the content of columns (a) to (f) of the tables:

(a) High-symmetry space group in the standard setting of axes defined by the international tables for x-ray crystallography.

(b) Brillouin-zone point relative to the order parameter. The adopted notation is the one of Zak's representation tables[17] and is specified in Refs. 12–14. The triclinic BZ was not considered in Zak's tables, and there is some variations in other available tables. We have labeled the points for this system in the same way as the corresponding points of the monoclinic (primitive) BZ.

(c) Nonferroic low-symmetry space groups identified by their standard international symbol. Similar to Ref. 14, the relative setting of the translations in the low- and high-symmetry phases is not specified. No ambiguity follows from the uniform notation. The actual setting can be deduced from the knowledge of the explicit translational symmetry changes associated to each BZ point, which are given in Ref. 66. In this column, the IR corresponding to the order parameter is specified between brackets by the symbol τ_i of the small representation referred to Zak's tables.

(d) Change in the number of atoms in the crystal's unit cell. As there is no change in the point group at a NFPT, the multiplication of the unit cell is uniquely determined for a given BZ point, as established in Ref. 12.

(e) Dimension of each relevant IR, this dimension being equal to the number of components of the order parameter.

(f) Type of free-energy expansion for the transition. The different types are explicited in Table VII.

For the cubic system an additional column indicates the "images" of the IR's (see Ref. 14 for their definition and use). The small number of distinct images in the other systems has made this column superfluous for Tables I–IV.

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