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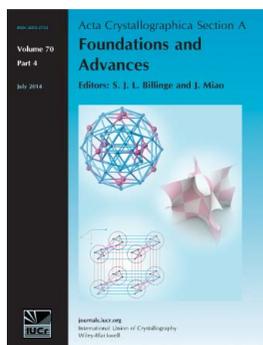
# Changes of physical properties in multiferroic phase transitions

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# Changes of physical properties in multiferroic phase transitions

Daniel B. Litvin

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Department of Physics, The Eberly College of Science, The Pennsylvania State University, Penn State Berks, PO Box 7009, Reading, Pennsylvania 19610, USA. Correspondence e-mail: u3c@psu.edu

The physical property coefficients that arise in a phase transition which are zero in the high-symmetry phase and nonzero in the low-symmetry phase are called *spontaneous coefficients*. For all 1601 Aizu species of phase transitions, matrices have been constructed which show the nonzero coefficients of a wide variety of magnetic and nonmagnetic physical properties including toroidal property coefficients in the high-symmetry phase and their corresponding spontaneous coefficients in the low-symmetry phase. It is also shown that these spontaneous coefficients provide for the distinction of and switching between nonferroelastic domain pairs.

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## 1. Introduction

A vast amount of literature exists on the derivation and tabulation of the form of individual physical property tensors invariant under magnetic and nonmagnetic crystallographic point groups (Birss, 1964; Sirotnin & Shaskolskaya, 1982; Nye, 1985; Brandmuller & Winter, 1985; Brandmuller *et al.*, 1986; Litvin & Litvin, 1991; *International Tables for Crystallography* (2003); and references contained in these sources).

To simultaneously present a set of physical property tensors, Nye (1985) constructed a single ten by ten *extended matrix*. This extended matrix combined the elastic tensor, piezoelectric tensor, thermal expansion tensor, dielectric susceptibility tensor, pyroelectric tensor and heat capacity/absolute temperature into a single matrix and its form invariant under each of the 32 nonmagnetic point groups was tabulated.

*Ferroic crystals* are anisotropic crystalline materials which exhibit structural phase transitions. The phase transition can be specified by two point groups **A** and **B**, where the group **B**, the point group of the lower symmetry phase, is a proper subgroup of group **A**, the point group of the higher symmetry phase. These phase transitions can be classified according to these two point groups. Each class is referred to as an *Aizu specie* and is denoted by a symbol **AFB**, where F is a symbol denoting ferroic (Aizu, 1969, 1970). There are 212 *nonmagnetic* Aizu species, *i.e.* species with **A** = **G**, where **G** is one of the 32 nonmagnetic crystallographic point groups. Let **1'** = {1, 1'} denote the time-inversion group consisting of the identity 1 and time inversion 1'. There are 1389 *magnetic* Aizu species which are subdivided into two subsets: 773 species with a group **A** = **G1'**, where **1'** is the time inversion group and 616 species with a group **A** = **G(H)** = **H** + (**G** – **H**)1', where **H** is a subgroup of index 2 of **G**, for a total of 1601 Aizu species (Litvin, 2009).

Janovec *et al.* (2010) used the extended matrix format of physical property tensors in their study of piezoelectric and electro-optic ferroic phase transitions. Characterizing each phase transition by one of the 212 nonmagnetic Aizu species, two extended matrices were constructed: the first matrix gave the form of the physical property tensors invariant under the point group **A** of the high-symmetry phase and the second gave the form invariant under the point group

**B** of the low-symmetry phase. In this second matrix, the nonzero components from the high-symmetry phase are given in black and the spontaneous coefficients, those components that are zero in the high-symmetry phase and nonzero in the low-symmetry phase, are given in red. This work was expanded by Litvin & Janovec (2014) to include the 1389 magnetic Aizu species where the extended matrices were enlarged to 13 by 13 matrices to include pyromagnetic, magneto-electric, magnetic susceptibility and piezomagnetic physical property tensors. Here, for each of the 1601 Aizu species, we again enlarge the extended matrices to 16 by 16 matrices. Each extended matrix combines twenty-five physical property tensors including now pyrotoroidic, electrotoroidic, magnetotoroidic and piezotoroidic tensors.

	$\Delta T$	$E_1 E_2 E_3$	$H_1 H_2 H_3$	$\sigma_1 \sigma_2 \sigma_3 \sigma_4 \sigma_5 \sigma_6$	$S_1 S_2 S_3$
$\Delta S$	C/T	$p^t$	$q^t$	$\beta^t$	$r^t$
$P_1$					
$P_2$	$p$	$\epsilon_0 X^e$	$\alpha^t$	$d$	$\theta$
$P_3$					
$M_1$					
$M_2$	$q$	$\alpha$	$X^m$	$\Lambda$	$\zeta$
$M_3$					
$\epsilon_1$					
$\epsilon_2$					
$\epsilon_3$	$\beta$	$d^t$	$\Lambda^t$	$s$	$\gamma$
$\epsilon_4$					
$\epsilon_5$					
$\epsilon_6$					
$T_1$					
$T_2$	$r$	$\theta^t$	$\zeta^t$	$\gamma^t$	$\tau$
$T_3$					

**Figure 1**  
 Representation of the extended matrix of physical property tensors and the physical properties which they relate. The nomenclature of these physical property tensors and physical properties is given in Table 1.

**Table 1**  
Nomenclature of physical properties and physical property tensors.

$\Delta S$	Change of entropy
$\Delta T$	Change of temperature
$T$	Absolute temperature
$E_i$	Electric field
$P_i$	Polarization
$H_i$	Magnetic field
$M_i$	Magnetization
$\sigma_m$	Stress
$\varepsilon_m$	Strain
$C$	Heat capacity
$T_i$	Toroidal moment
$S_i$	Toroidal field
$i, j$	1, 2, 3
$m, n$	1, 2, 3, 4, 5, 6
$r_i$	Pyrotoroidic coefficients
$r_i^t$	Toroidalcaloric coefficients
$T_{ij}^t$	Toroidic susceptibility
$\epsilon_{ij}^e$	Dielectric susceptibility coefficients
$X_{ij}^m$	Magnetic susceptibility coefficients
$s_{mn}$	Elastic compliance coefficients
$p_i$	Pyroelectric coefficients
$p_i^t$	Electrocaloric coefficients
$q_i$	Pyromagnetic coefficients
$q_i^t$	Magnetocaloric coefficients
$\beta_m$	Thermal expansion coefficients
$\beta_m^t$	Heat of deformation coefficients
$\alpha_{ij}$	Magnetolectric coefficients (direct effect)
$\alpha_{ij}^t$	Magnetolectric coefficients (inverse effect)
$d_{im}$	Piezoelectric coefficients (direct effect)
$d_{im}^t$	Piezoelectric coefficients (inverse effect)
$\Lambda_{im}$	Piezomagnetic coefficients (direct effect)
$\Lambda_{im}^t$	Piezomagnetic coefficients (inverse effect)
$\theta_{ij}$	Electrotoroidic coefficients (direct effect)
$\theta_{ij}^t$	Electrotoroidic coefficients (inverse effect)
$\zeta_{ij}$	Magnetotoroidic coefficients (direct effect)
$\zeta_{ij}^t$	Magnetotoroidic coefficients (inverse effect)
$\gamma_{im}$	Pyzotoroidic coefficients (direct effect)
$\gamma_{im}^t$	Pyzotoroidic coefficients (inverse effect)

**2. Spontaneous property tables<sup>1</sup>**

The extended matrices of the spontaneous property tables represent a set of equations that relate physical properties of the ferroic material. For the physical properties considered in this paper a representation of this set of equations is given in Fig. 1, giving only the symbols of the physical properties and of the physical property tensors. Table 1 gives the terminology of these physical properties and physical property tensors, and Table 2 the transformational properties of the physical property tensors in Jahn (1949) notation.

In the spontaneous property tables, for each of the 1601 Aizu species **AFB** we give two extended matrices representing the symmetry-allowed components of physical property tensors invariant under point-group symmetry **A** and under point-group symmetry **B**. The extended matrix of symmetry **B** is given in the setting of symmetry **A**. The two matrices associated with the spontaneous coefficient table of the Aizu specie  $6_22_12_1F3_22_x$  are shown in Fig. 2. On the left is the extended matrix of physical property tensors invariant under the group  $6_22_x2_1$  with entries only in black. On the right is the extended matrix of physical property tensors invariant under the group  $3_22_x$  where the nonzero components invariant under  $6_22_x2_1$  are given in black and the spontaneous coefficients, those components that are zero under  $6_22_x2_1$  and nonzero under  $3_22_x$  are given in red.

<sup>1</sup> The spontaneous property tables are available from the IUCr electronic archives (Reference: KX5026) and at <http://www.bk.psu.edu/faculty/litvin/Download.html>.

**Table 2**  
Jahn notation: transformational properties of the property tensors in Fig. 1.

$V$  denotes a polar vector,  $a$  is a scalar which inverts under time inversion,  $e$  is a scalar which inverts under spatial inversion and [ ] denotes symmetrization of the contents within the brackets.

1	V	aeV	[V <sup>2</sup> ]	aV
V	[V <sup>2</sup> ]	aeV <sup>2</sup>	V[V <sup>2</sup> ]	aV <sup>2</sup>
aeV	aeV <sup>2</sup>	[V <sup>2</sup> ]	aeV[V <sup>2</sup> ]	eV <sup>2</sup>
[V <sup>2</sup> ]	V[V <sup>2</sup> ]	aeV[V <sup>2</sup> ]	[[V <sup>2</sup> ] <sup>2</sup> ]	aV[V <sup>2</sup> ]
aV	aV <sup>2</sup>	eV <sup>2</sup>	aV[V <sup>2</sup> ]	[V <sup>2</sup> ]

**3. Distinction of and switching between two nonferroelastic domains**

The two point groups **A** and **B** in an Aizu specie **AFB** can represent, as originally introduced (Aizu, 1969, 1970), the point groups of the higher- and lower-symmetry phases in a structural phase transition of a ferroic crystal. As we show in this section, the two point groups of some Aizu species can also be related to a pair of nonferroelastic domains and the spontaneous coefficients of these Aizu species play a central role in the distinction and switching of the two nonferroelastic domains.

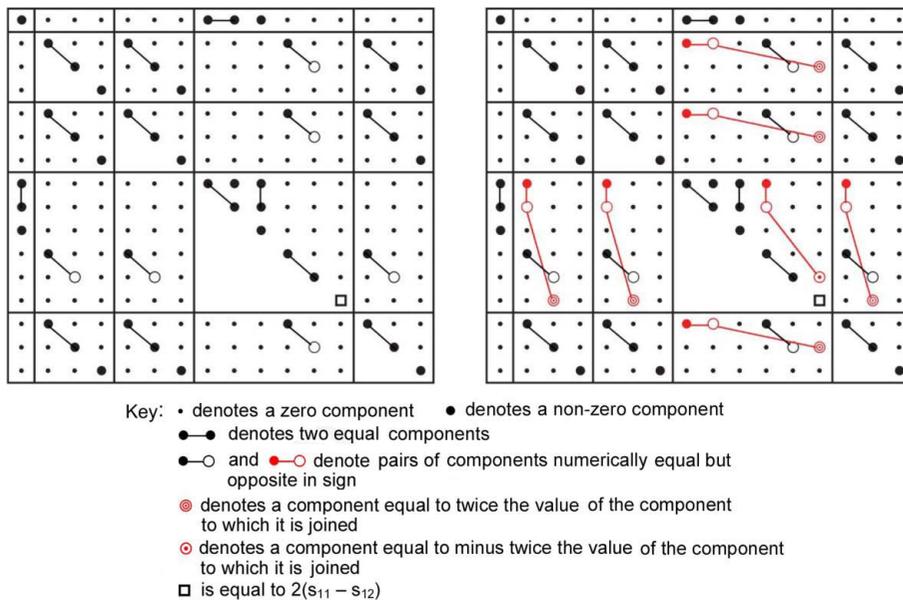
Consider a phase transition between phases of point-group symmetry **A** and **B**. The crystal splits into  $n = |\mathbf{A}|/|\mathbf{B}|$  single-domain states denoted by  $S_1, S_2, \dots, S_n$ . Writing the coset decomposition of **A** with respect to **B** as  $\mathbf{A} = \mathbf{B} + a_2\mathbf{B} + \dots + a_n\mathbf{B}$ , we have  $S_i = a_i S_1, i = 1, 2, \dots, n$ , i.e. the orientation of the  $i$ th domain  $S_i$  is related to the orientation of domain  $S_1$  by the element  $a_i$  of the coset decomposition, and  $\mathbf{B}_i = a_i\mathbf{B}_1a_i^{-1}$  is the symmetry group of the  $i$ th domain. A domain pair is denoted by  $(S_i, S_k)$  and the twin law  $\mathbf{J}_{ik}$  of a domain pair  $(S_i, S_k)$  is defined (Janovec, 1981) as

$$\mathbf{J}_{ik} = (\mathbf{B}_i \cap \mathbf{B}_k + a_{ik}(\mathbf{B}_i \cap \mathbf{B}_k)),$$

where  $a_{ik}$  is an element that interexchanges the two domains, i.e.  $a_{ik}S_i = S_k$  and  $a_{ik}S_k = S_i$ .

The two domains in a nonferroelastic domain pair  $(S_i, S_k)$  by definition possess the same spontaneous strain and the twin law of a nonferroelastic domain pair is then of the form  $\mathbf{J}_{ik} = \mathbf{B}_i + a_{ik}\mathbf{B}_i$ , where  $\mathbf{B}_i$  is the symmetry group of  $S_i$  and  $a_{ik}$  can be chosen such that  $a_{ik}^2 = 1$ , the identity element of  $\mathbf{B}_i$  (Litvin & Janovec, 2004, 2006). A nonferroelastic domain pair twin law is then defined by two groups,  $\mathbf{J}_{ik}$  and a proper subgroup  $\mathbf{B}_i$  of index 2, and can then be associated with the Aizu specie  $\mathbf{J}_{ik}\mathbf{FB}_i$ .

The tensor properties of the domain  $S_i$  are given in the extended matrix of the symmetry  $\mathbf{B}_i$  in the spontaneous tensor property table of the specie  $\mathbf{J}_{ik}\mathbf{FB}_i$ . The tensor properties of the domain  $S_k = a_{ik}S_i$  are



**Figure 2**

Spontaneous property table for  $6_z2_x2_1F3_z2_x$ . The nonzero tensor components in the high-symmetry phase are given in black in the extended matrix on the left and also in black in the low-symmetry phase extended matrix on the right. The *spontaneous coefficients*, those coefficients that are zero in the high-symmetry phase and nonzero in the low-symmetry phase, are given in red. The extended matrix is symmetric about its main diagonal.

given in the same extended matrix of symmetry  $\mathbf{B}_i$  with all spontaneous property coefficients multiplied by  $-1$  (Janovec & Přivratská, 2003; Litvin & Janovec, 2006). Consequently, the tensor distinction of a nonferroelastic pair of domains ( $S_i, S_k$ ), whose twin law is  $\mathbf{J}_{ik} = \mathbf{B}_i + a_{ik}\mathbf{B}_k$ , is given by the spontaneous coefficients of the spontaneous property table of the Aizu specie  $\mathbf{J}_{ik}\mathbf{F}\mathbf{B}_i$ .

The switching of two domains is driven by the difference in their free energy (Schmid, 2003), which in turn depends on the difference in the physical properties of the two domains. For pairs of nonferroelastic domains, because their tensor properties differ by  $-1$  for all spontaneous property coefficients of the Aizu specie  $\mathbf{J}_{ik}\mathbf{F}\mathbf{B}_i$  and are the same for all others, the difference in their free enthalpy depends only on the spontaneous property coefficients. Consequently, *switching of nonferroelastic domains with twin law  $\mathbf{J}_{ik} = \mathbf{B}_i + a_{ik}\mathbf{B}_k$  is associated only with those physical properties related by the spontaneous property coefficients of the Aizu specie  $\mathbf{J}_{ik}\mathbf{F}\mathbf{B}_i$ .*

As an example, consider the phase transition between a high-symmetry phase of point group  $\mathbf{A} = 6_z2_x2_1$  and a low-symmetry phase of point-group symmetry  $\mathbf{B} = 3_z2_x$ . There are two nonferroelastic domains and in the twin law of this nonferroelastic domain pair,  $\mathbf{J}_{12} =$

$\mathbf{B}_1 + a_{12}\mathbf{B}_1$ , we have  $\mathbf{J}_{12} = 6_z2_x2_1$ ,  $a_{12} = 6_z$  and  $\mathbf{B}_1 = 3_z2_x$ . The spontaneous tensor property table of the Aizu specie  $\mathbf{J}_{12}\mathbf{F}\mathbf{B}_1 = 6_z2_x2_1F3_z2_x$  is given in Fig. 2. The tensor distinction is given by the spontaneous property coefficients, *i.e.* by piezoelectric, piezomagnetic, piezotoroidic, and elastic compliance coefficients. As an example of switching, consider the piezoelectric coefficients  $d_{11} = -d_{12} = -2d_{26}$ . We have the ferroelastic–ferroelectric switching in Dauphiné twins, where the difference in free energy related to these piezoelectric coefficients is proportional to  $(E_1\sigma_{11} - E_1\sigma_{22} - 2E_2\sigma_{12})$ . Switching has been demonstrated in Dauphiné twins by using a stress  $\sigma_{11}$  and an electric field  $E_1$  (Laughner *et al.*, 1979).

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