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On the Symmetry Analysis of Surface Induced Effects

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The changes in the components of a wide variety of tensor physical properties, including piezomagnetic, piezomagnetic, magnetoelectric properties and toroidic properties, on traversing from the bulk to the surface of a crystalline material are explicitly tabulated.

Keywords Symmetry theory; physical properties

1. Introduction

Using symmetry theory Eliseev et al. [1] showed how symmetry breaking inevitably present in the vicinity of any surface gives rise to spontaneous surface piezomagnetic, piezoelectric and magnetoelectric effects in nanomaterials. Eliseev [2] then provided a symmetry analysis of these surface induced effects for all bulk non-magnetic and magnetic symmetries. This analysis specified the existence or non-existence of bulk ferromagnetic, linear magnetoelectric, piezomagnetic, ferroelectric and piezoelectric properties and the surface induced symmetries.

We extend this analysis by 1) providing the material coefficients that transform as components of the physical property tensors of these and other properties which are invariant under each bulk symmetry and 2) the explicit changes in these material coefficients, i.e. the surface induced effects, due to the symmetry breaking on traversing from the bulk symmetry to the surface symmetry. This information is presented in terms of *extended matrices of multiple tensor properties* introduced in Section 2. The results of this extended analysis is given in the *Tables of Induced Surface Effects* the content of which is detailed in Section 3.

2. Extended Matrices of Multiple Tensor Properties

Physical properties of anisotropic crystalline materials can be described by material coefficients that transform as components of tensors of various ranks. The matrix form of the physical property tensor is determined by the point group symmetry of the crystalline material and the internal symmetry of the property [3]. A wide variety of individual

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‡The complete *Tables of Induced Surface Effects* are available as Supplemental material online, and also at http://www.bk.psu.edu/faculty/litvin/Download.html

Table 1
Excerpt from the index of the *Tables of Induced Surface Effects*

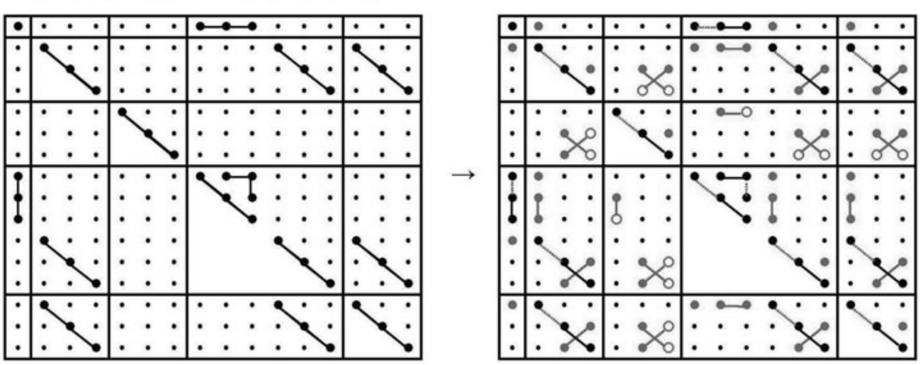
	Surface Orientation		
	(100) $\perp$ x	(110) $\perp$ xy	(111) $\perp$ xyz
Bulk Symmetry	Surface Symmetry		
$2_x 3_{xyz}$	2_x	1	3_{xyz}
$m_z\bar{3}_{xyz}$	$m_y m_z 2_x$	m_z	3_{xyz}
$m_z'\bar{3}_{xyz}'$	$m_y' m_z' 2_x$	m_z'	3_{xyz}
$\bar{4}_z 3_{xyz} m_{xy}$	$m_{yz} m_{\bar{y}z} 2_x$	$m_{\bar{x}y}$	$3_{xyz} m_{\bar{x}y}$
$\bar{4}_z' 3_{xyz} m_{xy}'$	$m_{yz}' m_{\bar{y}z}' 2_x$	$m_{\bar{x}y}'$	$3_{xyz} m_{\bar{x}y}'$
$4_z 3_{xyz} 2_{xy}$	4_x	2_{xy}	3_{xyz}
$4_z' 3_{xyz} 2_{xy}'$	$4_x'$	$2_{xy}'$	3_{xyz}

Note. The bulk symmetry is given in the left-hand-side column and the surface symmetry at the intersection of the bulk symmetry line and the surface orientation column.

physical property tensors invariant under non-magnetic and magnetic point groups with various internal symmetries have been derived and are available in print [4–10] or in computerized tabulations [11–14]. Nye [15] has shown how to simultaneously present the matrix form of multiple tensor properties: A single 10 by 10 extended matrix of a material's elastic coefficients, piezoelectric coefficients, thermal expansion coefficients, permittivities, pyroelectric coefficients, and heat capacity/absolute temperature was constructed and the form of this extended matrix invariant under one point group of each of the 32 non-magnetic point group types was tabulated.

Table 2
Two extended matrices of components of physical property tensors

4-(z)3(xyz)m(xy) → m(yz)m(y-z)2(x)



Note. The left-hand-side matrix is of components of physical property tensors invariant under the bulk symmetry $\bar{4}_z 3_{xyz} m_{xy}$ and the right-hand-matrix of components of physical property tensors invariant under the point group $m_{yz} m_{\bar{y}z} 2_x$, the point group of the surface of orientation (100).

Janovec et al. [16,17] have used an extended matrix format of material coefficients in their study of the changes in material coefficients during changes in symmetry in piezoelectric and electrooptic ferroics: For each of the 212 non-magnetic Aizu species [18], **A***F***B**, two extended matrices were constructed: The first gave the extended matrix of material coefficients invariant under the point group **A**, the point group of the so-called parent phase, and a second giving the extended matrix of the material coefficients invariant under the lower point group **B**, the point group of the ferroic phase. The two extended matrices are presented side-by-side. In the second extended matrix, invariant under the symmetry of the ferroic phase, those coefficients that were non-zero in the parent phase are given in black, and those coefficients that are zero in the parent phase and non-zero in the ferroic phase are given in red. The changes in the material coefficients during the change in symmetry is consequently emphasized and is visually self-evident. We shall detail, in the following section, the use of two extended matrices and color coding to provide an analogous tabulation of the symmetry analysis of surface induced effects in crystals.

3. Symmetry Analysis of Surface Induced Effects

This symmetry analysis focuses on the change in the components of physical property tensors between those invariant under the bulk point group symmetry of a crystal and those invariant under the point group symmetry of crystal surfaces of various orientations. In Table 1 we show an excerpt from the index, which is the same as in [2], of the *Tables of Induced Surface Effects*. The bulk symmetry is given in the left-hand-side column and the surface symmetry at the intersection of the bulk symmetry line and the surface orientation column. For each surface symmetry, two extended matrices are given. In Table 2 we give the two extended matrices of the components of physical property tensors: the left-hand-side matrix is of components of physical property tensors invariant under the bulk symmetry $\bar{4}_z 3_{xyz} m_{xy}$ and the right-hand-matrix of components of physical property tensors invariant under the point group $m_{yz} m_{\bar{y}z} 2_x$, the point group of the surface of orientation (100). Those coefficients which were non-zero in the parent phase are given in black, and those coefficients that are zero in the parent phase and non-zero in the ferroic phase are given in grey.

In the two extended matrices, see Table 2, each set of material coefficients within each bordered rectangle are components of a physical property tensor relating physical properties. These extended matrix physical property tensors and physical properties are set out in Table 3, with the meaning of all symbols given in Table 4. For example, the linear magnetoelectric effect $M_i = \alpha_{ij} E_j$ has the magnetoelectric coefficients α_{ij} of the magnetoelectric physical property tensor relate the components E_j of the electric field, to the components M_i of magnetization.

In Table 5 we list the symbols used in the extended matrix physical property tensors in Table 2 to signify properties of and relationships among the material coefficients of the property tensors (a complete list of such symbols for use in the *Tables of Induced Surface Effects* is given with the tables.) For example, ●—○ denotes that two material coefficients are zero components in the bulk symmetry and non-zero components numerically equal but opposite in sign in the surface symmetry. This is the case for two pair of magnetoelectric coefficients α_{ij} in Table 2. The pair of coefficients α_{22} and α_{33}, and the pair of coefficients α_{23} and α_{32}, are zero in the bulk symmetry $\bar{4}_z 3_{xyz} m_{xy}$ and are non-zero numerically equal but opposite in sign, $\alpha_{22} = -\alpha_{33}$ and $\alpha_{23} = -\alpha_{32}$, under the surface symmetry $m_{yz} m_{\bar{y}z} 2_x$.

Table 3
Symbols of the extended matrix physical property tensors and the physical properties to which they relate

	ΔT	$E_1\ E_2\ E_3$	$H_1\ H_2\ H_3$	$\sigma_1\ \sigma_2\ \sigma_3\ \sigma_4\ \sigma_5\ \sigma_6$	$S_1\ S_2\ S_3$
ΔS	C/T	p^t	q^t	β^t	r^t
P_1 P_2 P_3	p	$\varepsilon_o X^e$	α^t	d	θ
M_1 M_2 M_3	q	α	X^m	Λ	ζ
ε_1 ε_2 ε_3 ε_4 ε_5 ε_6	β	d^t	Λ^t	s	γ
T_1 T_2 T_3	r	θ^t	ζ^t	γ^t	τ

Table 4
Meaning of the physical property and physical property tensor symbols of Table 3

ΔS	change of entropy	$\varepsilon_o X^e{}_{ij}$	dielectric susceptibility coefficients
ΔT	change of temperature	$X^m{}_{ij}$	magnetic susceptibility coefficients
T	absolute temperature	s_{mn}	elastic compliance coefficients
E_i	electric field	p_i	pyroelectric coefficients
P_i	polarization	$p^t{}_i$	electrocaloric coefficients
H_i	magnetic field	q_i	pyromagnetic coefficients
M_i	magnetization	$q^t{}_i$	magnetocaloric coefficients
σ_m	stress	β_m	thermal expansion coefficients
ε_m	strain	$\beta^t{}_m$	heat of deformation coefficients
C	heat capacity	α_{ij}	magnetoelectric coefficients (direct effect)
T_i	toroidal moment	$\alpha^t{}_{ij}$	magnetoelectric coefficients (inverse effect)
S_i	toroidal field	d_{im}	piezoelectric coefficients (direct effect)
$i,j = 1,2,3$		$d^t{}_{im}$	piezoelectric coefficients (inverse effect)
$m,n = 1,2,3,4,5,6$		Λ_{im}	piezomagnetic coefficients (direct effect)
		$\Lambda^t{}_{im}$	piezomagnetic coefficients (inverse effect)
r_i	pyrotoroidal coefficients	θ_{ij}	electrotoroidic coefficients (direct effect)
$r_i{}^t$	toroidalcaloric coefficients	$\theta^t{}_{ij}$	electrotoroidic coefficients (inverse effect)
τ_{ij}	toroidic susceptibility	ζ_{ij}	magnetotoroidic coefficients (direct effect)
		$\zeta^t{}_{ij}$	magnetotoroidic coefficients (inverse effect)
		γ_{im}	piezotoroidic coefficients (direct effect)
		$\gamma^t{}_{im}$	piezotoroidic coefficients (direct effect)

Table 5
Symbols used in the extended matrices of Table 2 to signify properties of and relationships among the material coefficients of the property tensors

Triangular matrices represent matrices symmetrical about the leading diagonal

	zero component
	non-zero component, no conditions on its value
	non-zero equal components
	zero component in the bulk symmetry , non-zero component in the surface symmetry
	zero components in the bulk symmetry, non-zero components and equal in the surface symmetry
	zero components in the bulk symmetry, non-zero components numerically equal but opposite in sign in the surface symmetry
	non-zero and equal components in the bulk symmetry, non-zero and not symmetry related in the surface symmetry

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References

1. E. A. Eliseev, A. N. Morozovska, M. D. Glinchuk, B. Y. Zaulychny, V. V. Skorokhod, and R. Blinc, Surface-induced piezomagnetic, piezoelectric, and linear magnetoelectric effects in nanosystems, *Phys. Rev.* **B82**, 085408 1–7 (2010).
2. E. A. Eliseev, Complete symmetry analyses of the surface-induced piezomagnetic, piezoelectric and linear magnetoelectric effects, *Ferroelectrics* **417**, 100–109 (2011).
3. H. A. Jahn, Note on the Bhagavantam-Suryanarayana method of enumerating the physical constants of crystals, *Acta Cryst.*, **2**, 30–31 (1949).
4. R. R. Birss, *Symmetry and Magnetism*, Amsterdam: North Holland, 1964.
5. D. E. Sands, *Vectors and Tensors in Crystallography*, Reading, MA: Addison-Wesley, 1982.
6. J. Brandmuller, and F. X. Winter, Influence of symmetry on the static and dynamic properties of crystals, *Z. Kristallogr.* **172**, 191–231 (1985).
7. H. Grimmer, General connections for the form of property tensors in the 122 Shubnikov point groups, *Acta Cryst.* **A47**, 226–232 (1991).
8. Yu Sirotin, and M. P. Shaskolskaya, *Fundamentals of Crystal Physics*, Moscow: Mir, 1982.
9. J. Brandmuller, H. Bross, W. G. Bauer, and F. X. Winter, Tables to accompany Brandmuller, J & Winter, FX: Influence of symmetry on the static and dynamic properties of crystals, *Z. Kristallogr.* **172**, 191–231 (1985) (second corrected edition with extension to non-crystallographic point groups (1986)).
10. A. Authier, *(editor) International tables for crystallography, Volume D: Physical Properties of Crystals*, Dordrecht: Kluwer Academic, (2003).

11. S. Y. Litvin, and D. B. Litvin, Rank 0,1,2, and 3 magnetic and non-magnetic physical property tensors, *Acta Cryst.* **A47**, 290–292 (1991).
12. S. V. Popov, Svirko, P. Yu, and N. I. Zheludev, *Susceptibility Tensors for Nonlinear Optics*, Bristol: Institute of Physics, (1995).
13. S. V. Popov, Svirko, P. Yu, and N. I. Zheludev, *Encyclopedia of Material Tensors on CD*, Chichester: John Wiley, (1999).
14. M. Ephraim, T. Jannsen, A. Janner, and A. Thiers, *Introduction to the accompanying software Tenχar, Section 1.2.7, in International Tables for Crystallography, Volume D: Physical properties of crystals*, A. Authier, ed., Kluwer Academic, Dordrecht, 2003, 62–69.
15. J. F. Nye, *Physical Properties of Crystals*, Oxford: Clarendon Press, 1985, Appendix E.
16. V. Janovec, M. Čmelik, and L. Machonský, Piezoelectric and electrooptic ferroics –qualitative domain and tensor characteristics, *Phase Transitions* **83**, 670–681 (2010).
17. V. Janovec, M. Čmelik, and L. Machonský, Piezoelectric species, http://palata.fzu.cz/species/piezo/
18. K. Aizu, Electrical, mechanical and electromechanical orders of state shifts in nonmagnetic ferroic crystals, *J. Phys. Soc. Japan* **32**, 1287–1301 (1972).