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OPTICAL AND X-RAY DISTINCTION OF FERROELECTRIC NON-FERROELASTIC DOMAINS

V. JANOVEC[*], L. RICHTEROVÁ[+], and D. B. LITVIN[x]

[*]Institute of Physics, Czechoslovak Academy of Sciences,
Na Slovance 2, 180 40 Prague 8, Czechoslovakia

[+]Comenius University, Faculty of Mathematics and Physics,
Mlynska dolina F1, 842 15 Bratislava, Czecho-Slovakia

[x]Department of Physics, The Pennsylvania State University
The Berks Campus, P.O. Box 7007, Reading, PA 1960-6009, U.S.A.

Abstract We show that there exist 17 possible relations (twin laws) between structures of two ferroelectric non-ferroelastic domains. For each twin law we indicate whether X-ray diffraction intensities from two domains equal or differ and give number of optical tensor components that can distinguish both domains. We list twin laws which appear in particular ferroelectric non-ferroelastic or partially ferroelastic phases.

INTRODUCTION

Domains are connected regions in which the low-symmetry structure acquires different orientation in space. When observed from one coordinate frame domains may exhibit different physical properties. If we chose two domains D_1 and D_2 then it is the spatial relation between their structures S_1 and S_2 that determines which properties would be the same and which would appear different in these two domains. It is, therefore, convenient to consider, instead of domains D_1 and D_2, only their strucrures S_1 and S_2. Two such structures, treated irrespectively of their coexistence and of domain shapes, form a *domain pair (DP)*[1]. A domain pair can be considered algebraically as an unordered set $\{S_1, S_2\}$ and geometrically as a superposition of structures S_1 and S_2.

Domain pairs can be divided into two basic classes: In a *non-ferroelastic domain pair* $\{S_1, S_2\}$ the structures S_1 and S_2 have the same (zero or non-zero) spontaneous deformation whereas in a *ferroelastic domain pair* they exhibit different spontaneous deformations. There is a close relation between this division and the older classification of twins[2,3,4] : non-ferroelastic DP's correspond to merohedry twins (or twins by twin-lattice symmetry) whereas ferroelastic twins correspond to pseudomerohedry twins (or twins by twin lattice quasi-symmetry).

Since the tensor of spontaneous deformation transforms in the same way as the optical indicatrix the structures of a ferroelastic DP can be easily distinguished in a polarizing microscope whereas the structures of an non-ferroelastic DP cannot be recognized in this way. Further, the reciprocal lattices of structures S_1 and S_2 in a ferroelastic DP have different orientation and therefore give rise to double spots in X-ray diffractograms. On the other hand, the same reciprocal lattice of structures S_1 and S_2 of a non-ferroelastic DP produces only single diffraction spots. It is then natural to ask whether the structures of a non-ferroelastic DP can exhibit differences in some other optical properties and whether they can produce diffraction spots of different intensities. In this contribution we answer these questions for an important subclass of non-ferroelastic DP's, namely for *ferroelectric domain pairs*, in which the structures S_1 and S_2 possess different spontaneous polarization differing in orientation or direction.

DOMAIN PAIRS AND TWIN LAWS

The relation between structures S_1 and S_2 in a DP, which we shall call the *twin law* of the DP, can be specified most conveniently by a dichromatic group[5] which has, for a non-ferroelastic DP, the simple form[6]

$$J = F + j'F , \tag{1}$$

where F is the symmetry group of S_1 and, simultaneously, of S_2 and j' is an operation that exchanges S_1 and S_2, i.e.,

$$j'S_1 = S_2 \quad , \quad j'S_2 = S_1 . \tag{2}$$

Group J expresses the symmetry of $\{S_1, S_2\}$, since operations of F leave both S_1 and S_2 invariant and operations from the left coset j'F exchange S_1 and S_2 but leave the domain pair invariant since $\{S_2, S_1\} = \{S_1, S_2\}$.

For a non-ferroelastic DP the groups J and F belong to the same crystal family. A ferroelectric DP (structures S_1 and S_2 differ in spontaneous polarization) is specified by a condition that either J is non-polar and F polar or both J and F are polar but their polar axes have different directions. For discussing tensorial distinction of domains a continuum description using point-group symmetries suffices: All possible twin laws (expressed by a dichromatic point group J) of non-ferroelastic ferroelectric domain pairs are given in the first column of Table I. The second column displays the symmetry F of both structures S_1 and S_2. We see that there are in all 17 non-ferroelastic ferroelectric twin laws. All groups J are non-polar hence spontaneous polarisation in two structures S_1 and S_2 is antiparallel.

X-RAY AND OPTICAL DISTINCTION OF DOMAINS

The twin law (1) allows one to deduce useful conclusions about X-ray diffraction from a non-ferroelastic domain structure[7]. Let I_1 and I_2 be the intensities of X-ray reflections per unit volume of structures S_1 and S_2 respectively. As long as Friedel's law is valid (the anomalous scattering is not taken into account) the equality $I_1 = I_2$ holds if the twinning operations j'F belong to the Laue symmetry of F. The set of intensities measured on two domains D_1 and D_2 is then identical with one that would be measured on a single crystal of the same volume. All twin laws fulfilling this condition are denoted = in the fourth column "difint" of the Table I. If twin operations j'F do not belong to the Laue symmetry of F then $I_1 \neq I_2$ and the intensity of a reflection depends on the fractional volume of domains D_1 and D_2. Such twin laws are denoted / in Table I.

The twin law (1) also determines which components of a material property tensor T are different in S_1 and S_2. These components, being invariant under the operations of F and changing sign under remaining operations j'F of J, transform as basis functions of the alternating representation D_a^J of J which subduces the identity representation in F. The components of the tensor T transform as a set of basis functions of a representation D^T. The number m^T of tensor components of T that discriminate structures S_1 and S_2 thus equals the multiplicity of D^{J}_{α} in D^{T}.

Using this procedure we have determined the number m^{T} for tensors describing the most important optical properties of crystals. The results are summarized in Table I where different tensors are denoted by the Jahn's symbols.

TABLE I Ferroelectric non-ferroelastic twin laws, X-ray intensities and numbers of distinct tensor components

J	F	D^{J}_{α}	difint	$\varepsilon[V^2]$	$V[V^2]$	$\varepsilon V\{V^2\}^2$	$\{V^2\}^2$
$\bar{1}'$	1	A_u	=	6	18	0	0
$2/m'$	2	A_u	=	4	8	0	0
$2'/m$	m	B_u	=	2	10	0	0
mmm'	mm2	B_{1u}	=	1	5	0	0
$mm'm$	m2m	B_{2u}	=	1	5	0	0
$m'mm$	2mm	B_{3u}	=	1	5	0	0
$4/m'$	4	A_u	=	2	4	0	0
$42'2'$	4	A_2	/	0	3	3	3
$4/m'mm$	4mm	A_{2u}	=	0	3	0	0
$\bar{3}'$	3	A_u	=	2	6	0	0
$32'$	3	A_2	/	0	4	4	4
$\bar{3}'m$	3m	A_{2u}	=	0	4	0	0
$\bar{6}'$	3	A''	/	2	4	2	4
$6/m'$	6	A_u	=	2	0	3	0
$62'2'$	6	A_2	/	0	3	3	2
$\bar{6}'m2'$	3m1	A_2	/	0	3	1	2
$6/m'mm$	6mm	A_{2u}	=	0	3	0	0

$\varepsilon[V^2]$ ...optical activity, $V[V^2]$ ...electrooptics,
$\varepsilon V\{V^2\}^2$ ...electrogyration, $[V^2]^2$ ...elastooptics.

As seen from Table I, for almost all twin laws there are several optical property tensors that can be used for domain distinction. Exceptional are twin laws J = $4/m'mm$, $\bar{3}'m$ and $6/m'mm$ in which domains can be discriminated just by different electrooptic coefficients. Results given in Table I apply not only to domain pairs but also to twins by merohedry with pyroelectric twin components that differ in direction of the polar direction.

Table II lists for each phase transition (G and F is the symmetry of the high-symmetry and low-symmetry phase, resp.) all twin laws J that can appear in the low-symmetry phase. Phase transitions are classified in columns "a" and "e" as non-ferroelastic (na) or partial ferroelastic (pa) and full ferroelectric (fe) or partial ferroelectric (pe) ones*.

Table II Distribution of twin laws J in ferroelectric partial (pa) and non-ferroelastic (na) phases

G	F	a	e	J
$\bar{1}$	1	na	fe	$\bar{1}'$
2/m	1	pa	fe	$\bar{1}'$
	2	na	fe	$2/m'$
	m	na	fe	$2'/m$
mmm	1	pa	fe	$\bar{1}'$
	2	pa	fe	$2/m'$
	m	pa	fe	$2'/m$
	2mm	na	fe	$m'mm$
	m2m	na	fe	$mm'm$
	mm2	na	fe	mmm'
4/m	1	pa	fe	$\bar{1}'$
	2	pa	pe	$2/m'$
	m	pa	fe	$2'/m$
	4	na	fe	$4/m'$
422	4	na	fe	$42'2'$
4/mmm	1	pa	fe	$\bar{1}'$
	2	pa	pe	$2/m'$
	m	pa	fe	$2'/m$
	mm2	pa	pe	mmm'
	4	na	pe	$4/m'$ $42'2'$
	4mm	na	fe	$4/m'mm$
$\bar{3}$	1	pa	fe	$\bar{1}'$
	3	na	fe	$\bar{3}'$
321	3	na	fe	$32'1$
312	3	na	fe	$312'$
$\bar{3}$m1	1	pa	fe	$\bar{1}'$
	2	pa	fe	$2/m'$
	m	pa	fe	$2'/m$
	3	na	pe	$\bar{3}'$ $32'1$ $3m'1$
	3m1	na	fe	$\bar{3}'m1$
$\bar{3}$1m	1	pa	fe	$\bar{1}'$
	2	pa	fe	$2/m'$
	m	pa	fe	$2'/m$
	3	na	pe	$3'$
$\bar{3}$1m	31m	na	fe	$\bar{3}'1m$
$\bar{6}$	3	na	fe	$\bar{6}'$
6/m	1	pa	fe	$\bar{1}'$
	2	pa	pe	$2/m'$
	m	pa	fe	$2'/m$
	3	na	pe	$\bar{3}'$ $6'$ $\bar{6}'$
	6	na	fe	$6/m'$
622	3	na	pe	$6'$ $32'1$ $312'$
	6	na	fe	$62'2'$
$\bar{6}$m2	3	na	pe	$312'$ $\bar{6}'$ $3m'1$
	3m1	na	fe	$\bar{6}'m2'$
$\bar{6}$2m	3	na	pe	$32'1$ $\bar{6}'$ $31m'$
	31m	na	fe	$\bar{6}'2'm$
6/mmm	1	pa	fe	$\bar{1}'$
	2	pa	pe	$2/m'$
	m	pa	fe	$2'/m$
	mm2	pa	pe	mmm'
	2mm	pa	fe	$m'mm$
	m2m	pa	fe	$mm'm$
	3	na	pe	$\bar{3}'$ $6'$ $\bar{6}'$ $32'1$ $312'$ $3m'1$ $31m'$
	3m1	na	pe	$\bar{3}'m1$ $6'mm'$ $\bar{6}'m2'$

TABLE II cont.

G	F	a	e	J
	31m	na	pe	3´1m
				6´m´m
				$\bar{6}'2'm$
	6	na	pe	6/m´
				62´2´
				6m´m´
	6mm	na	fe	6/mmm´
$m\bar{3}$	1	pa	fe	$\bar{1}'$
	2	pa	pe	2/m´
	m	pa	fe	2´/m
	mm2	pa	fe	mmm´
	3	pa	fe	$\bar{3}'$
432	4	pa	fe	42´2´
	3	pa	fe	32´
$\bar{4}3m$	3	pa	pe	3m´
$m\bar{3}m$	1	pa	fe	$\bar{1}'$
	2	pa	pe	2/m´
	m	pa	fe	2´/m
	mm2	pa	pe	mmm´
	2mm	pa	fe	m´mm
	4	pa	pe	4/m´
				42´2´
				4m´m´
	4mm	pa	fe	4/m´mm
	3	pa	pe	$\bar{3}'$
	3m	pa	fe	$\bar{3}'m$

Distinction of ferroelectric non-ferroelastic domains by means of optical activity has been studied experimentally e.g., on lead germanate[9] (twin law $J=\bar{3}'$) and in triglycine sulphate[10] (J=2/m´). A detailed discussion of optical distinction of ferroelectric domains in various materials has been given in Ref. 11.

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