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Macroscopic symmetries and domain configurations of engineered domain structures

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Abstract

We describe a procedure for determining possible macroscopic symmetries of a multidomain ferroic crystal. The domain structure is represented by ferroic domain states and by their partial volumes which define its *domain configuration*. If such a crystal is exposed to external field(s), all possible domain states may no longer have equal free energy. Except for special cases, all states with same free energy are equivalent under the maximal subgroup H of the prototypic point group G that leaves the field(s) invariant; such states form an H-*orbit*. Provided that the ferroic crystal contains all states from a single H-orbit, and if these states occupy equal partial volumes, a *coherent domain configuration* arises. Its averaged symmetry is given by the *stabilizer of the* H-*orbit*, i.e. by the maximal subgroup of G transforming the H-orbit of states into itself. Within the model used, the possible macroscopic symmetry of the crystal is either the symmetry of a coherent domain configuration or an intersection of some of these symmetries.

The procedure is demonstrated on rhombohedral perovskite crystals for which all macroscopic symmetries and the external fields that produce coherent configurations are given.

1. Introduction

In recent years, domain engineering has emerged as a new direction in materials research. Interest in domain engineering has been stimulated by the discovery that rhombohedral ferroelectric single crystals of relaxor-based $Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PZN-PT) acquire an extremely high value of both the piezoelectric coefficient d_{33} and the electromechanical coupling k_{33} after being poled in an electric field along the [001] direction of the prototypic cubic phase [1–4]. The resulting domain structure was found to have very low fatigue [5]. These properties make the engineered PZN-PT crystals a highly promising transducer material in comparison to Pb(Zr, Ti)O_3 ceramics, the current piezoelectric material of choice.

A similar but less intense enhancement of electromechanical properties was observed in perovskite $BaTiO_3$ crystals [6] and in potassium niobate ($KNbO_3$) crystals [7].

Besides the practical importance, such results also raise the question of the possible macroscopic symmetries of engineered domain structures and their domain configurations (DCs). In the case of the rhombohedral PZN-PT crystals it was assumed that in an electric field along [001] four equivalent domain states are enhanced at the expense of the others, giving rise to the macroscopic symmetry 4mm [8]. However, a more recent work has suggested that the symmetry of these crystals can be orthorhombic mm2, or even lower [9, 10]. In this connection, Erhart and Cao [11, 12] analysed an effective macroscopic symmetry and physical properties of ferroelastic twins. Fousek *et al* [13] have deduced macroscopic symmetries of rhombohedral PZN-PT crystals in which domain states occupy equal partial volumes. For each symmetry the authors listed two DCs. Here we give a complete solution for both equal and unequal partial volumes.

In this paper we present a general method for deriving all possible macroscopic symmetries of the multidomain structures of a given ferroic phase. The necessary mathematical background is briefly reviewed in section 2 (lemmas 1 and 2) and two main concepts are explained: an *orbit of domain states* under a given point group and the *class of equivalent divisions of the set of* all *domain states into* such *orbits*. Each orbit identifies a distinct free energy level while each class specifies a possible symmetry. In section 3 we give a necessary condition (condition 1) for a multidomain crystal to exhibit certain macroscopic symmetry, and a criterion (condition 2) that the symmetry must fulfil. We introduce the concept of a *coherent domain configuration* and suggest that any multidomain crystal satisfying condition 1 can be considered as a 'composition' of coherent configurations. In section 4 it is shown that the only tetragonal symmetry that the rhombohedral PZN-PT crystals can have is 4mm. The basic algorithm for determining macroscopic symmetries of multidomain ferroic phases, together with the procedure for deriving DCs for each symmetry, is described in section 5. In section 6 we discuss external fields that can induce distinct coherent configurations.

2. Mathematical background

Multidomain crystals are characterized by the presence of distinct domain states. In the following we shall neglect the disorientations of the ferroelastic domains. We shall work with the ferroic single-domain states (orientational states [14]) resulting from the phase transition $\mathsf{G} \searrow \mathsf{F}$, where G and F are the prototypic and the ferroic point group, respectively. Throughout the paper, such states will be referred to merely as *states*.

An action of the group G *on a set* M of elements $a, b, c, \ldots$ is a mapping $\mathsf{G} \times M \mapsto M$ which to any operation g from G, $g \in \mathsf{G}$, and to any element a from M, $a \in M$, assigns an element b from M, $b \in M$; this is written briefly as $g\,a = b$. Such a mapping must fulfil two additional conditions [15]: (i) $e\,a = a$ for any $a \in M$ and the identity e of G; and (ii) $(gh)\,a = g\,(h\,a)$ for all $g, h \in \mathsf{G}$ and any $a \in M$.

One defines *the stabilizer* $\mathrm{Stab}_{\mathsf{G}}(a)$ of an element $a \in M$ in the group G as the maximal subgroup of G whose operations leave a fixed, i.e. $g \in \mathsf{G}$ belongs to $\mathrm{Stab}_{\mathsf{G}}(a)$ if $g\,a = a$. Similarly, one introduces the stabilizer $\mathrm{Stab}_{\mathsf{H}}(a)$ of a in any subgroup H of G, $\mathsf{H} \subseteq \mathsf{G}$. One can show that the stabilizer $\mathrm{Stab}_{\mathsf{H}}(a)$ is an intersection $\mathsf{H} \cap \mathrm{Stab}_{\mathsf{G}}(a) = \mathrm{Stab}_{\mathsf{H}}(a)$.

The concept of group action on a set will be used in two different instances. In one of them, the elements of the set M are all possible states resulting from the phase transition $\mathsf{G} \searrow \mathsf{F}$. The action of G on such a set is *transitive* (see e.g. [16]): for each two states there is an operation $g \in \mathsf{G}$ taking one state into the other. The individual states will be numbered as follows: select some state as a reference one and denote its symmetry by F_1. Then one can

establish a one-to-one correspondence between the states and the left cosets of F_1 in G [14,17]. The group G is a disjoint union of all these left cosets [18], and so one can write

$$\mathsf{G} = \mathsf{F}_1 + g_2\,\mathsf{F}_1 + \cdots + g_n\,\mathsf{F}_1, \tag{1}$$

where the operation g_i, $i = 2, \ldots, n$, is called the representative of the ith coset. (For the representative of the first coset we choose the identity, i.e. $g_1\,\mathsf{F}_1 = e\,\mathsf{F}_1 = \mathsf{F}_1$.) The index $n := [\mathsf{G} : \mathsf{F}_1]$ of the subgroup F_1 in G gives the number of all possible states; since the point group G is finite, n equals $|\mathsf{G}|/|\mathsf{F}_1|$, where $|\mathsf{G}|$ and $|\mathsf{F}_1|$ are the numbers of the operations lying in G and F_1, respectively. Denoting by $\langle 1\rangle$ the selected state of the symmetry F_1, we put $\langle 2\rangle = g_2\,\langle 1\rangle, \ldots, \langle n\rangle = g_n\,\langle 1\rangle$.

The symmetry of the ith state, $\langle i\rangle = g_i\,\langle 1\rangle$, is described by its stabilizer $\mathsf{F}_i := \mathrm{Stab}_{\mathsf{G}}(\langle i\rangle)$ that is conjugate to F_1 in G, $\mathsf{F}_i = g_i\,\mathsf{F}_1\,g_i^{-1}$. The intersection (2) of all the stabilizers $\mathsf{F}_1, \ldots, \mathsf{F}_n$ (which may but need not be pairwise distinct) is the maximal subgroup of G that leaves each state fixed. It is denoted as [19]

$$\mathsf{core}\,\mathsf{F} := \mathsf{F}_1 \cap \mathsf{F}_2 \cap \cdots \cap \mathsf{F}_n. \tag{2}$$

If F_1 is normal in G, i.e. $g\mathsf{F}_1 g^{-1} = \mathsf{F}_1$ for any $g \in \mathsf{G}$, then $\mathsf{core}\,\mathsf{F} = \mathsf{F}_1 = \cdots = \mathsf{F}_n$. We note that the group $\mathsf{core}\,\mathsf{F}$ gives the *minimal symmetry of* a *multidomain ferroic crystal* whose prototypic and ferroic symmetries are G and F, respectively. Other possible crystal symmetries must be among supergroups $\mathsf{H}, \mathsf{K}, \ldots,$ of $\mathsf{core}\,\mathsf{F}$.

The central notion of the exposition below is the H-*orbit of a state* $\langle i\rangle$, where H is a subgroup of G: it is defined as a set whose elements are generated by applying consecutively all operations of H to the state $\langle i\rangle$. To obtain the H-orbit one can use the representatives of distinct cosets in the decomposition of the group H with respect to the stabilizer of $\langle i\rangle$ in H, $\mathrm{Stab}_{\mathsf{H}}(\langle i\rangle) = \mathsf{H} \cap \mathrm{Stab}_{\mathsf{G}}(\langle i\rangle) = \mathsf{H} \cap \mathsf{F}_i$:

$$\mathsf{H} = \mathrm{Stab}_{\mathsf{H}}(\langle i\rangle) + h_2\mathrm{Stab}_{\mathsf{H}}(\langle i\rangle) + \cdots + h_q\mathrm{Stab}_{\mathsf{H}}(\langle i\rangle), \qquad q = |\mathsf{H}|/|\mathrm{Stab}_{\mathsf{H}}(\langle i\rangle)|. \tag{3}$$

The H-orbit consists of q states $\langle i_1\rangle = \langle i\rangle, \langle i_2\rangle = h_2\langle i\rangle, \ldots, \langle i_q\rangle = h_q\langle i\rangle$. The group H acts on the orbit transitively: the operation $h_k h_l^{-1}$ takes the state $\langle i_l\rangle$ into $\langle i_k\rangle$. For such an orbit we will use a composed symbol consisting of the group symbol and the number of some state within the orbit, say $\langle i_1\rangle$, separated by a star, i.e. $\mathsf{H}\star i_1$. Such a symbol is not unique, since $\mathsf{H}\star i_1 = \mathsf{H}\star i_l$, $l = 2, \ldots, q$. One can see that the set of all n states is the G-orbit of the state $\langle 1\rangle$, i.e. $\{1, 2, \ldots, n\} := \{\langle 1\rangle, \langle 2\rangle, \ldots, \langle n\rangle\} = \mathsf{G}\star 1 = \mathsf{G}\star 2 = \cdots = \mathsf{G}\star n$.

Any two orbits $\mathsf{H}\star i$, $\mathsf{H}\star j$ either coincide or have no state in common. The following lemma holds [15]:

Lemma 1. *Suppose that an action of the point group* G *is defined on a set* $M = \{a, b, c, \ldots\}$. *For any* $\mathsf{H} \subseteq \mathsf{G}$ *the set* M *is either an* H*-orbit or a union of mutually disjoint* H*-orbits.*

Any subgroup H of G thus gives a division of the orbit $\mathsf{G}\star 1 = \{1, \ldots, n\}$ into H-orbits of states. In two cases such division yields a trivial result: either an H-orbit contains all the states, i.e. $\mathsf{H}\star 1 = \mathsf{G}\star 1$, or each H-orbit consists of a single state, i.e. $\mathsf{H} \subseteq \mathsf{core}\,\mathsf{F}$.

An H-orbit of states has a clear physical meaning: suppose a multidomain crystal is exposed to an external macroscopic field whose symmetry group contains a subgroup H of the prototypic group G. If H is a supergroup of $\mathsf{core}\,\mathsf{F}$, there exists an orbit $\mathsf{H}\star i \neq \{\langle i\rangle\}$. Select from it another state $h\,\langle i\rangle$, $h \in \mathsf{H}$. Being invariant under H, the applied field must have the same effect on both the states, $\langle i\rangle$ and $h\,\langle i\rangle$. Therefore, their free energy in the field must be equal. In general, every H-orbit of states represents a distinct level of free energy in any macroscopic field for which the intersection of its symmetry group with G equals H.

In the other application of the group action, the elements of the set M are all orbits $\mathsf{H}\star i$, where $i = 1, \ldots, n$ and $\mathsf{core}\,\mathsf{F} \subseteq \mathsf{H} \subseteq \mathsf{G}$. One can check that operations of G permute such

orbits among themselves: an operation $g \in \mathsf{G}$ takes an orbit $\mathsf{H} \star i_1$ into the H^g-orbit of the state $g\,\langle i_1\rangle$ consisting of q states $g\langle i_1\rangle, \ldots, g\langle i_q\rangle$, where $\mathsf{H}^g = g\,\mathsf{H}\,g^{-1}$ and H are conjugate in G. Accordingly, the division of $\{1, \ldots, n\}$ into H-orbits is transformed by g into the division of $\{1, \ldots, n\}$ into H^g-orbits. The stabilizer $\mathrm{Stab}_{\mathsf{G}}(\mathsf{H} \star i_1)$ of the orbit $\mathsf{H} \star i_1$ in G contains all such operations $g \in \mathsf{G}$ that permute the states of $\mathsf{H} \star i_1$, thus leaving the orbit as a whole invariant. One can see that the stabilizer of the H^g-orbit of $g\,\langle i_1\rangle$ is $g\,\mathrm{Stab}_{\mathsf{G}}(\mathsf{H} \star i_1)\,g^{-1}$—a subgroup of G conjugate to $\mathrm{Stab}_{\mathsf{G}}(\mathsf{H} \star i_1)$. Note that $\mathrm{Stab}_{\mathsf{G}}(\mathsf{H} \star i_1)$ must contain H.

For arbitrary subgroups H_1 and H_2 of G, the divisions of the set $\{1, \ldots, n\}$ into H_1- and H_2-orbits are called *equivalent* if some operation $g \in \mathsf{G}$ takes every orbit $\mathsf{H}_1 \star i$ into an orbit $\mathsf{H}_2 \star j$. The physical characteristics of two equivalent divisions are the same since the stabilizer of an H_1-orbit and the stabilizer of the corresponding H_2-orbit are conjugate in G. If H_1 and H_2 themselves are conjugate, the divisions of $\{1, \ldots, n\}$ into H_1- and H_2-orbits must be equivalent. Thus one gets the following lemma:

Lemma 2. *There are at most as many non-equivalent divisions of the set of n states into group orbits as there are distinct classes of conjugate subgroups in* G *containing the group* $\mathsf{core\ F}$.

As we will see, each division gives a possible macroscopic symmetry of the multidomain ferroic crystal.

The exposition given above is illustrated on a PZN-PT crystal. To distinguish point groups from the symmetry operations involved, we type respective symbols in different fonts. For example, m_z will denote the reflection in a plane perpendicular to the z-axis while the monoclinic point group containing this reflection and the identity will be written, using the international symbol, as $\mathsf{m_z}$, i.e. $\mathsf{m_z} = \{1, m_z\}$. We use the following notation (in square brackets on the right-hand side the direction of a rotation axis is given): $4_z = 4_{[001]}, 4_x = 4_{[100]}$, $4_y = 4_{[010]}$, $3_{xyz} = 3_{[111]}$, $3_{x\bar{y}z} = 3_{[\bar{1}\bar{1}1]}$, $3_{x\bar{y}\bar{z}} = 3_{[1\bar{1}\bar{1}]}$, $3_{\bar{x}y\bar{z}} = 3_{[\bar{1}1\bar{1}]}$, $2_{x\bar{y}} = 2_{[\bar{1}10]}$, $2_{y\bar{z}} = 2_{[0\bar{1}1]}$, $2_{z\bar{x}} = 2_{[10\bar{1}]}$, $2_{xy} = 2_{[110]}$, $2_{yz} = 2_{[011]}$ and $2_{zx} = 2_{[101]}$.

A PZN-PT crystal with the prototypic and the ferroic point group $\mathsf{m\bar{3}m}$ and $\mathsf{3m}$, respectively, has eight possible states that differ in polarization—a primary order parameter of the phase transition $\mathsf{m\bar{3}m} \searrow \mathsf{3m}$. The polarizations of the states are parallel to the threefold axes. By $\langle 1\rangle$ we denote the state with the polarization vector oriented along [111]. Its stabilizer F_1 is $\mathsf{3_{xyz}m_{x\bar{y}}}$, and so we rewrite (1) as follows:

$$\begin{aligned}\mathsf{m\bar{3}m} = {} & \mathsf{3_{xyz}m_{x\bar{y}}} + 2_z\,\mathsf{3_{xyz}m_{x\bar{y}}} + 2_x\,\mathsf{3_{xyz}m_{x\bar{y}}} + 2_y\,\mathsf{3_{xyz}m_{x\bar{y}}} \\ & + \bar{1}\,\mathsf{3_{xyz}m_{x\bar{y}}} + m_z\,\mathsf{3_{xyz}m_{x\bar{y}}} + m_x\,\mathsf{3_{xyz}m_{x\bar{y}}} + m_y\,\mathsf{3_{xyz}m_{x\bar{y}}}. \qquad (4)\end{aligned}$$

To each state we assign the sequential number of the respective coset in the decomposition (4) (see figure 1). The symmetry of the states is $\mathsf{F}_1 = \mathsf{F}_5 = \mathsf{3_{xyz}m_{x\bar{y}}}$, $\mathsf{F}_2 = \mathsf{F}_6 = \mathsf{3_{\bar{x}\bar{y}z}m_{x\bar{y}}}$, $\mathsf{F}_3 = \mathsf{F}_7 = \mathsf{3_{x\bar{y}\bar{z}}m_{xy}}$, and $\mathsf{F}_4 = \mathsf{F}_8 = \mathsf{3_{\bar{x}y\bar{z}}m_{xy}}$. There are four non-ferroelastic pairs, $\{1, 5\}$, $\{2, 6\}$, $\{3, 7\}$ and $\{4, 8\}$, in which both states have the same spontaneous deformation. The polarizations in each pair are antiparallel: $\boldsymbol{P}^{(1)} = -\boldsymbol{P}^{(5)} = (P, P, P)$, $-\boldsymbol{P}^{(2)} = \boldsymbol{P}^{(6)} = (P, P, -P)$, $-\boldsymbol{P}^{(3)} = \boldsymbol{P}^{(7)} = (-P, P, P)$ and $-\boldsymbol{P}^{(4)} = \boldsymbol{P}^{(8)} = (P, -P, P)$, where $\boldsymbol{P}^{(i)}$ is the polarization of the ith state and $P > 0$.

To produce orbits of the states under a subgroup of $\mathsf{m\bar{3}m}$ one can apply relevant operations to the eight polarization vectors shown in figure 1. From the figure one directly reads that each non-ferroelastic pair is an orbit of the triclinic group $\bar{1} = \{1, \bar{1}\}$. Thus the set $\{1, \ldots, 8\}$ splits into four $\bar{1}$-orbits, $\{1, 5\} \cup \{2, 6\} \cup \{3, 7\} \cup \{4, 8\}$. Similarly, one checks that $\{1, 2\}$, $\{3, 4\}$, $\{5, 6\}$ and $\{7, 8\}$ are 2_z-orbits which define another division of $\{1, \ldots, 8\}$.

Inspecting figure 1 one can find the stabilizer of a given orbit of any subgroup of $\mathsf{m\bar{3}m}$. One can see, for example, that the $\bar{1}$-orbits $\{1, 5\}$, $\{2, 6\}$, $\{3, 7\}$ and $\{4, 8\}$ are stabilized by

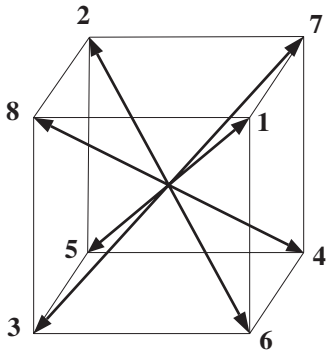

Figure 1. Eight states of a ferroelectric rhombohedral PZN-PT crystal.

the trigonal groups $\overline{3}_{xyz}2_{x\bar{y}}/m_{x\bar{y}}$, $\overline{3}_{\bar{x}yz}2_{x\bar{y}}/m_{x\bar{y}}$, $\overline{3}_{x\bar{y}\bar{z}}2_{x\bar{y}}/m_{x\bar{y}}$, $\overline{3}_{x\bar{y}\bar{z}}2_{xy}/m_{xy}$ and $\overline{3}_{\bar{x}y\bar{z}}2_{xy}/m_{xy}$, respectively. The stabilizers of all the 2_z-orbits coincide with the orthorhombic group $m_{xy}m_{x\bar{y}}2_z$.

3. Macroscopic symmetry of ferroic crystals. Coherent and incoherent domain configurations

A multidomain crystal has an averaged macroscopic symmetry H if a matrix of any property tensor $\overline{\boldsymbol{U}} = (\overline{U}_{j_1,j_2,\ldots})$ is invariant under the group H. The symmetry H of the crystal can be observed due to a volume-averaging effect of macroscopic field(s) which is incorporated into an overall response of the domain structure to these fields. We will assume that the contribution of domain bulks to the crystal properties is dominant so that other contributions can be neglected. Any effective property tensor $\overline{\boldsymbol{U}}$ can be then written as a function of tensor properties $\boldsymbol{U}^{(1)}, \ldots, \boldsymbol{U}^{(n)}$ of the states $\langle 1\rangle, \ldots, \langle n\rangle$, respectively, which are multiplied by the respective partial volumes V_i/V, $i = 1, \ldots, n$, i.e. $\overline{\boldsymbol{U}} = \overline{\boldsymbol{U}}((V_1/V)\,\boldsymbol{U}^{(1)}, \ldots, (V_n/V)\,\boldsymbol{U}^{(n)})$, where V is the crystal volume. For brevity, we write $\overline{\boldsymbol{U}} = \overline{\boldsymbol{U}}((V_i/V)\,\boldsymbol{U}^{(i)})$. The macroscopic symmetry H implies that if the original coordinate system is transformed by an operation $h \in \mathsf{H}$ into a new one, then tensor properties of the crystal must be the same in both the systems so that $\overline{\boldsymbol{U}}((V_i/V)\,\boldsymbol{U}^{(i)}) = \overline{\boldsymbol{U}} = \overline{\boldsymbol{U}}' = \overline{\boldsymbol{U}}((V_i'/V)\,\boldsymbol{U}'^{(i)})$. The operation h will not change any partial volume V_i/V (since it is a scalar), but instead of the property $\boldsymbol{U}^{(i)}$ of the state $\langle i\rangle$ one will get in the new coordinate system the property $\boldsymbol{U}^{(k_i)}$ of the state $\langle k_i\rangle = h^{-1}\langle i\rangle$. Consequently, $\overline{\boldsymbol{U}}((V_i/V)\,\boldsymbol{U}^{(i)}) = \overline{\boldsymbol{U}}((V_i/V)\,\boldsymbol{U}^{(k_i)})$. After rearranging the arguments we obtain that $\overline{\boldsymbol{U}}((V_i/V)\,\boldsymbol{U}^{(i)}) = \overline{\boldsymbol{U}}((V_1/V)\,\boldsymbol{U}^{(k_1)}, \ldots, (V_n/V)\,\boldsymbol{U}^{(k_n)}) = \overline{\boldsymbol{U}}((V_{l_1}/V)\,\boldsymbol{U}^{(1)}, \ldots, (V_{l_n}/V)\,\boldsymbol{U}^{(n)}) = \overline{\boldsymbol{U}}((V_{l_i}/V)\,\boldsymbol{U}^{(i)})$, where $\langle l_i\rangle = h\,\langle i\rangle$. This holds for all $h \in \mathsf{H}$, and so $\overline{\boldsymbol{U}}((V_i/V)\,\boldsymbol{U}^{(i)}) = \overline{\boldsymbol{U}}((V_{l_i}/V)\,\boldsymbol{U}^{(i)}) = \cdots = \overline{\boldsymbol{U}}((V_{m_i}/V)\,\boldsymbol{U}^{(i)})$, where all the states $\langle i\rangle, \langle l_i\rangle, \ldots, \langle m_i\rangle$ form an orbit $\mathsf{H} \star i$. If the stabilizer of the tensor property $\boldsymbol{U}^{(1)}$ of the state $\langle 1\rangle$ equals F_1, the tensor $\boldsymbol{U}$ will acquire distinct values $\boldsymbol{U}^{(1)}, \ldots, \boldsymbol{U}^{(n)}$ in all n states. Therefore, no matter what the form of the function $\overline{\boldsymbol{U}} = \overline{\boldsymbol{U}}((V_i/V)\,\boldsymbol{U}^{(i)})$ is, the partial volumes $V_i/V, V_{l_i}/V, \ldots, V_{m_i}/V$ must be equal. One gets a necessary condition for a multidomain crystal to exhibit a macroscopic symmetry H:

Condition 1. *All states within an arbitrary single orbit under* H *must have equal partial volumes.*

We note that this condition will be valid also if besides $(V_i/V)\,\boldsymbol{U}^{(i)}$, $i = 1, \ldots, n$, one introduces other arguments to the function $\overline{\boldsymbol{U}} = \overline{\boldsymbol{U}}((V_i/V)\,\boldsymbol{U}^{(i)})$ in order to include further

structural characteristics such as the presence of domain walls or an effective influence of defects.

One can see that the basic information needed for analysing a macroscopic symmetry of a multidomain crystal is the knowledge of all possible states and of their partial volumes that give their relative weights (if some state is absent, its weight is zero). Owing to this, we shall adopt a simple model in which a multidomain crystal is represented by its DC defined by the domain states and their weights.

We shall examine a ferroic crystal consisting of a large number of domains. As we are neglecting any structural defects and domain walls, we put $V_1 + \cdots + V_n = V$. We approximate the function $\overline{\boldsymbol{U}} = \overline{\boldsymbol{U}}((V_i/V)\,\boldsymbol{U}^{(i)})$ by a statistical average over the properties of the individual states, $\overline{\boldsymbol{U}} \approx \sum_{i=1}^{n}(V_i/V)\,\boldsymbol{U}^{(i)}$. If the crystal has the macroscopic symmetry H, then the set of n states splits into $p \geqslant 1$ H-orbits, i.e. $\{1,\ldots,n\} = \mathsf{H}\star i_1 \cup \cdots \cup \mathsf{H}\star i_p$, where $\mathsf{H}\star i_k = \{\langle i_k\rangle = \langle i_{k,1}\rangle, \ldots, \langle i_{k,r_k}\rangle\}$, $k = 1,\ldots,p$. The partial volumes $V_{k,l}/V$, $l = 1,\ldots,r_k$, of all states within the orbit $\mathsf{H}\star i_k$ must be equal, i.e. $V_{k,l}/V = v_k$ for all l. A DC of such crystal can be specified by the p orbits $\mathsf{H}\star i_k$ and by the p-tuple $[u_1,\ldots,u_p]$, where $u_k = r_k v_k$ is the total partial volume occupied by the r_k states within the kth orbit, and $\sum_{k=1}^{p} u_k = 1$.

In general, there may exist two or more subgroups of G under which the set of n states will split into same orbits. The same relationships among partial volumes of individual states will then follow for each symmetry. This happens e.g. with the groups $\mathsf{2}_\mathsf{z}$ and $\mathsf{m}_{\mathsf{xy}}\mathsf{m}_{\mathsf{x\bar{y}}}\mathsf{2}_\mathsf{z}$: in either case, the equalities $V_1 = V_2$, $V_3 = V_4$, $V_5 = V_6$ and $V_7 = V_8$ are obtained.

Such ambiguity stems from the fact that for any subgroup K of G the stabilizer $\mathrm{Stab}_\mathsf{G}(\mathsf{K}\star i_l)$ of a K-orbit $\mathsf{K}\star i_l$, $l = 1,\ldots,q$, may be a supergroup of K. Therefore, another group $\overline{\mathsf{K}}$ may be contained in $\mathrm{Stab}_\mathsf{G}(\mathsf{K}\star i_l)$ for all l such that each K-orbit will be a $\overline{\mathsf{K}}$-orbit, too. Take e.g. $\mathsf{K} = \overline{\mathsf{3}}_{\mathsf{xyz}}$. Both $\overline{\mathsf{3}}_{\mathsf{xyz}}$-orbits $\overline{\mathsf{3}}_{\mathsf{xyz}}\star 1 = \{1,5\}$ and $\overline{\mathsf{3}}_{\mathsf{xyz}}\star 2 = \{2,3,4,6,7,8\}$ are also orbits of other two groups, $\overline{\mathsf{K}} = \mathsf{3}_{\mathsf{xyz}}\mathsf{2}_{\mathsf{x\bar{y}}}$ and their stabilizer $\overline{\mathsf{3}}_{\mathsf{xyz}}\mathsf{2}_{\mathsf{x\bar{y}}}/\mathsf{m}_{\mathsf{x\bar{y}}}$. Then $V_1 = V_5$ and $V_2 = V_3 = V_4 = V_6 = V_7 = V_8$ for each symmetry.

The maximal subgroup of G whose orbits are K-orbits as well is the intersection of their stabilizers. It will be called the *closure* K^c *of* K with respect to the action of G on the set of n states:

$$\mathsf{K}^\mathsf{c} = \mathrm{Stab}_\mathsf{G}(\mathsf{K}\star i_1) \cap \cdots \cap \mathrm{Stab}_\mathsf{G}(\mathsf{K}\star i_q) \supseteq \mathsf{K}. \tag{5}$$

The basic property of the closure operation (5) is that the closure of any $\mathsf{K} \subseteq \mathsf{G}$ coincides with the closure of itself, i.e. $(\mathsf{K}^\mathsf{c})^\mathsf{c} = \mathsf{K}^\mathsf{c}$. Further, the closure of a conjugate $\mathsf{K}^g = g\,\mathsf{K}\,g^{-1}$, $g \in \mathsf{G}$, to K is the conjugate of the closure K^c, $(\mathsf{K}^g)^\mathsf{c} = g\,\mathsf{K}^\mathsf{c}g^{-1} = (\mathsf{K}^\mathsf{c})^g$. (Other useful properties are stated in section 5.)

In the model adopted, a macroscopic symmetry H of a multidomain crystal is determined solely by its DC: H is the maximal subgroup of G which admits existing equalities among the partial volumes of individual states. Nevertheless, a possible symmetry H can be characterized independently of the DC. According to the condition 1 a set of all states, whose non-zero weights are equal, must be invariant under H. Since the set $\mathcal{M}_0$ containing the states with a zero weight, and the union of all sets each consisting of states with the same weight, are complementary in $\{1,\ldots,n\}$, $\mathcal{M}_0$ is invariant under H, too. Owing to lemma 1, each set splits into H-orbits in a unique way. The maximality of H implies that there is no supergroup $\overline{\mathsf{H}}$ of H for which every H-orbit will be also an $\overline{\mathsf{H}}$-orbit, i.e.

Condition 2. *Any macroscopic symmetry* H *of a multidomain crystal is an intersection of the stabilizers of all its orbits, i.e.* $\mathsf{H} = \mathsf{H}^\mathsf{c}$.

Every subgroup K of G fulfilling condition 2 will be called a *principal symmetry* of such a crystal. In the examples discussed above, the closure $\mathsf{2}_\mathsf{z}^\mathsf{c} = \mathsf{m}_{\mathsf{xy}}\mathsf{m}_{\mathsf{x\bar{y}}}\mathsf{2}_\mathsf{z}$ and $\overline{\mathsf{3}}_{\mathsf{xyz}}^\mathsf{c} = (\mathsf{3}_{\mathsf{xyz}}\mathsf{2}_{\mathsf{x\bar{y}}})^\mathsf{c} =$

$\overline{3}_{xyz}2_{x\bar{y}}/m_{x\bar{y}}$ are principal symmetries of the PZN-PT crystals while 2_z, $\overline{3}_{xyz}$ and $3_{xyz}2_{x\bar{y}}$ are not. In the approximation used, all principal symmetries exhaust possible macroscopic symmetries of a multidomain crystal.

Condition 2 establishes *a one-to-one correspondence between the principal symmetries and the divisions of the set of all possible states into group orbits* introduced in section 2: as stated above, the intersection of stabilizers of all orbits contained in such division gives a principal symmetry of the crystal. Conversely, each principal symmetry $\mathsf{K} = \mathsf{K}^c$ determines a division of the set of all states into K-orbits.

Condition 2 allows one to determine possible macroscopic symmetries of a multidomain crystal without considering its DC. In order to find DCs with a given principal symmetry H it is instructive to specify explicitly what the relationship is between the set of states, occupying a non-zero volume, and the principal symmetry H. Suppose that in the crystal there are present m states with q distinct weights, say $v_1, \ldots, v_q$, $q \leqslant m \leqslant n$. One can divide the m states into q sets $\mathcal{M}_1, \ldots, \mathcal{M}_q$, where each $\mathcal{M}_j$ contains all states whose weight is v_j. The group H must leave any of these q sets invariant (cf condition 1), and so it must be contained in the stabilizer $\mathrm{Stab}_{\mathsf{G}}(\mathcal{M}_j)$ of each set $\mathcal{M}_j$. Since the symmetry of the domain configuration is given by the intersection of all these stabilizers, then

$$\mathrm{Stab}_{\mathsf{G}}(\mathcal{M}_1) \cap \cdots \cap \mathrm{Stab}_{\mathsf{G}}(\mathcal{M}_q) = \mathsf{H}. \tag{6}$$

Putting $M = \mathcal{M}_j$ and replacing G with $\mathrm{Stab}_{\mathsf{G}}(\mathcal{M}_j)$ in lemma 1, one infers that $\mathcal{M}_j$ is either an H-orbit, say $\mathsf{H} \star i_{j,1}$, or it splits (uniquely) into several H-orbits, $\mathsf{H} \star i_{j,1}, \ldots, \mathsf{H} \star i_{j,s_j}$. In the former case $\mathrm{Stab}_{\mathsf{G}}(\mathcal{M}_j) = \mathrm{Stab}_{\mathsf{G}}(\mathsf{H} \star i_{j,1}) \supseteq \mathsf{H}$. In the latter case the intersection $\mathsf{L}_j := \bigcap_{l=1}^{s_j} \mathrm{Stab}_{\mathsf{G}}(\mathsf{H}\star i_{j,l})$ of the s_j stabilizers is the maximal subgroup of G that transforms each orbit $\mathsf{H}\star i_{j,l}$ into itself. The group L_j leaves the set $\mathcal{M}_j$ invariant, and so $\mathrm{Stab}_{\mathsf{G}}(\mathcal{M}_j) \supseteq \mathsf{L}_j \supseteq \mathsf{H}$. Using (6) one obtains that

$$\bigcap_{j=1}^{q} \mathrm{Stab}_{\mathsf{G}}(\mathcal{M}_j) := \mathrm{Stab}_{\mathsf{G}}(\mathcal{M}_1) \cap \cdots \cap \mathrm{Stab}_{\mathsf{G}}(\mathcal{M}_q) = \bigcap_{j=1}^{q} \mathsf{L}_j = \bigcap_{j=1}^{q} \bigcap_{l=1}^{s_j} \mathrm{Stab}_{\mathsf{G}}(\mathsf{H} \star i_{j,l}) = \mathsf{H}. \tag{7}$$

Since the stabilizer of every H-orbit contains H, equation (7) agrees with condition 2.

Condition 1 implies that if in a multidomain crystal exhibiting the symmetry H some state is missing, then its whole H-orbit must be absent. And further, if any state of an H-orbit is present, then all states of this orbit appear and must occupy equal partial volumes in the crystal. In the simplest case only states belonging to a single H-orbit, say $\mathsf{H}\star i_k$, will be involved. The corresponding DC will be called *coherent* and will be denoted by $\langle i_{k,1}, \ldots, i_{k,r_k}\rangle$, where $v_k = 1/r_k$. Its symmetry H must equal the stabilizer of the kth H-orbit, $\mathrm{Stab}_{\mathsf{G}}(\mathsf{H} \star i_k) = \mathsf{H}$.

A coherent DC $\langle i_{l,1}, \ldots, i_{l,r_l}\rangle$, $1 \leqslant l \leqslant p$, is said to be *trivial* if the orbit $\mathsf{H} \star i_l$ contains either all n states or just one state $\langle i_l\rangle$. In the former case all the states have equal weights and the crystal exhibits the prototypic symmetry G while the latter case represents a single-domain crystal with the symmetry F_{i_l}.

In the first example given above there are four coherent DCs $\varsigma_k^{(z)} := \langle 2k-1, 2k\rangle$, $k = 1, \ldots, 4$, of the symmetry $m_{xy}m_{x\bar{y}}2_z$. Two of them are shown schematically in figure 2, the other two are obtained through the reflection m_z. Each $\varsigma_k^{(z)}$ can be specified by the vectors $v_k \boldsymbol{P}^{(2k-1)}$ and $v_k \boldsymbol{P}^{(2k)}$ ($v_k = \frac{1}{2}$) whose sum gives the effective polarization $\overline{\boldsymbol{P}}(\varsigma_k^{(z)})$. It is represented by the dashed–dot line parallel to the z-axis.

In the other example one obtains two coherent DCs of the symmetry $\overline{3}_{xyz}2_{x\bar{y}}/m_{x\bar{y}}$, $\vartheta_1^{(r)} = \langle 1, 5\rangle$ and $\vartheta_2^{(r)} = \langle 2, 3, 4, 6, 7, 8\rangle$ (see figures 3(*a*), (*b*)). Similarly to in figure 2, each DC is represented by the vectors that are parallel to the polarizations of the states involved

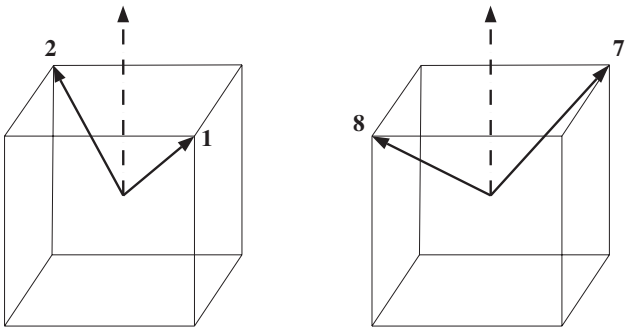

Figure 2. Two coherent DCs of the symmetry $\mathsf{H} = \mathsf{m}_{xy}\mathsf{m}_{x\bar{y}}2_z$: (*a*) $\varsigma_1^{(z)} = \langle 1, 2\rangle$; (*b*) $\varsigma_4^{(z)} = \langle 7, 8\rangle$.

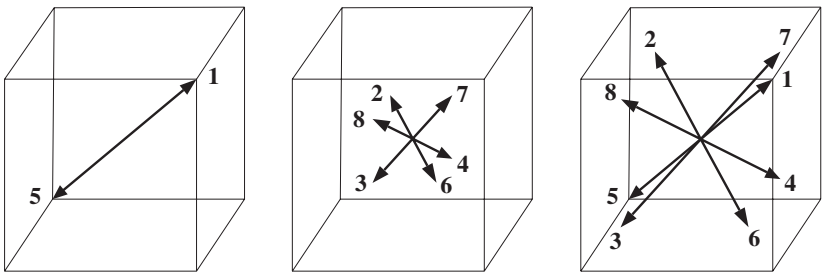

Figure 3. Coherent DCs of the symmetry $\mathsf{H} = \bar{3}_{xyz}2_{x\bar{y}}/\mathsf{m}_{x\bar{y}}$ and a mixed one: (*a*) $\vartheta_1^{(r)} = \langle 1, 5\rangle$; (*b*) $\vartheta_2^{(r)} = \langle 2, 3, 4, 6, 7, 8\rangle$; (*c*) $\frac{1}{3}\vartheta_1^{(r)} \sqcup \frac{2}{3}\vartheta_2^{(r)}$ (scale 3 : 1).

and whose length is proportional to the corresponding partial volume (for all coherent DCs the same scale is used).

A multidomain crystal exhibiting a macroscopic symmetry H may contain several H-orbits of states. The DC $D_{\{u\}}$ of such a crystal can be looked at as a formal composition of the coherent DCs each corresponding to a distinct H-orbit:

$$D_{\{u\}} = u_1\langle i_{1,1}, \ldots, i_{1,r_1}\rangle \sqcup \cdots \sqcup u_p\langle i_{p,1}, \ldots, i_{p,r_p}\rangle, \tag{8}$$

where '$\sqcup$' means 'coexists with', and the partial volumes $u_1, \ldots, u_p$, yield the weights of distinct coherent configurations. According to (7), the symmetry of the DC $D_{\{u\}}$ is the intersection of the stabilizers $\mathrm{Stab}_{\mathsf{G}}(\mathsf{H} \star i_l)$ of all those orbits $\mathsf{H} \star i_l$ for which $u_l \neq 0$:

$$\bigcap_{\substack{l=1 \\ u_l \neq 0}}^{p} \mathrm{Stab}_{\mathsf{G}}(\mathsf{H} \star i_l) = \mathsf{H}. \tag{9}$$

Therefore, any macroscopic symmetry of a multidomain crystal is either the symmetry of a coherent DC or an intersection of several such symmetries. We note that for a given symmetry H there may exist several DCs that differ in a set of the zero weights. If at least two weights do not vanish, two cases can be recognized: either the crystal involves a coherent DC $\langle i_{k_0,1}, \ldots, i_{k_0,r_{k_0}}\rangle$ such that $\mathsf{H} = \mathrm{Stab}_{\mathsf{G}}(\mathsf{H} \star i_{k_0})$, or not.

Table 1. Macroscopic symmetries of the rhombohedral PZN-PT crystals.

DC	Macroscopic symmetry {no of states}
Coherent[a]	$\mathsf{m\bar{3}m}\{8^*\}$, $\mathsf{\bar{4}3m}\{4\}$, $\mathsf{\bar{3}2/m}\{2,6\}$, $\mathsf{m_{xy}m_{x\bar{y}}m_z}\{4\}$, $\mathsf{4mm}\{4\}$, $\mathsf{3m}\{1^*,3\}$, $\mathsf{m_{xy}m_{x\bar{y}}2_z}\{2\}$, $\mathsf{2_{xy}m_{x\bar{y}}m_z}\{2\}$
Incoherent[b]	$\mathsf{2_{x\bar{y}}/m_{x\bar{y}}}\{4,6\}$, $\mathsf{2_{x\bar{y}}}\{4\}$, $\mathsf{m_{x\bar{y}}}\{2,3\}$, $\mathsf{m_z}\{4\}$, $\mathsf{\bar{1}}\{6\}$, $\mathsf{1}\{3\}$

[a] The trivial coherent configurations.
[b] Number of states given for the minimal incoherent configurations.

In the former case, $D_{\{u\}}$ will be called a *mixed configuration*. It may contain, in addition to the coherent DC $\langle i_{k_0,1},\ldots,i_{k_0,r_{k_0}}\rangle$, any of the remaining $p-1$ coherent configurations. It is almost obvious that for every non-trivial coherent DC there exists a mixed DC of the same symmetry, and vice versa. A simple example of a mixed DC consisting of two coherent DCs of the symmetry $\mathsf{\bar{3}_{xyz}2_{x\bar{y}}/m_{x\bar{y}}}$ is shown in figure 3(*c*). Less trivial is a mixed DC of the symmetry $\mathsf{m_{xy}2_{x\bar{y}}m_z}$, $\overline{u}_1\varrho_1^{(x\bar{y})}\sqcup\overline{u}_2\mu_1^{(z)}:=\overline{u}_1\langle 3,8\rangle\sqcup\overline{u}_2\langle 1,2,5,6\rangle$, where the symmetry $\mathrm{Stab}_{\mathsf{m\bar{3}m}}(\mathsf{m_{xy}2_{x\bar{y}}m_z}\star 1)$ of $\mu_1^{(z)}$ is $\mathsf{m_{xy}m_{x\bar{y}}m_z}\supset\mathsf{m_{xy}2_{x\bar{y}}m_z}$ (cf table 2).

In the latter case, $D_{\{u\}}$ will be referred to as an *incoherent configuration*. Its symmetry is always lower than the symmetry of any coherent DC included. An incoherent DC of the symmetry H is *minimal* if after any of the $q\leqslant p$ coherent DCs involved is omitted, the new DC thus obtained has a higher symmetry $\mathsf{H}'\supset\mathsf{H}$. Unless minimal itself, any incoherent DC can be reduced, by expelling of one or more coherent DCs, to a minimal configuration with the same symmetry. Such a reduction need not be unique.

The stabilizers of all $\mathsf{\bar{1}}$-orbits (cf section 2) imply that for the principal symmetry $\mathsf{\bar{1}}$ there exist only incoherent DCs which involve either any three or all four coherent DCs of a trigonal symmetry $\mathsf{\bar{3}2/m}$. Among them only the incoherent configuration containing all eight states is not minimal. Another example of an incoherent DC provides a multidomain PZN-PT crystal in which the states $\langle 1\rangle$, $\langle 5\rangle$ and $\langle 6\rangle$ occupy equal volumes. This DC which is composed of three trivial coherent DCs, $\frac{1}{3}\varpi_1^{(r)}\sqcup\frac{1}{3}\varpi_2^{(r)}\sqcup\frac{1}{3}\varpi_2^{(z)}$, is minimal and has the symmetry $\mathsf{m_{x\bar{y}}}$ as can be seen in table 3.

We note that as a consequence of lemma 1, any p-tuple $[u_1,\ldots,u_p]$ of the weights of the p coherent DCs, which specifies a DC of the symmetry H, must be such that condition 1 will not be satisfied for any supergroup K of H: the most general DC of the symmetry $\mathsf{2_{x\bar{y}}}$ is $D_{\{u\}}=u_1\langle 1,5\rangle\sqcup u_2\langle 2,6\rangle\sqcup u_3\langle 3,8\rangle\sqcup u_4\langle 4,7\rangle$ (cf table 3). Using tables 2 and 3 one can check that for $u_1=u_2$ the symmetry of $D_{\{u\}}$ would be $\mathsf{m_{xy}2_{x\bar{y}}m_z}$, while for $u_3=u_4$ one would observe the symmetry $\mathsf{2_{x\bar{y}}/m_{x\bar{y}}}$. Accordingly, it must be $u_1\neq u_2$ and $u_3\neq u_4$.

4. Tetragonal symmetry and corresponding domain configurations in rhombohedral PZN-PT single crystals

To find which tetragonal symmetries fulfil condition 2 one has to determine all orbits of the relevant groups. Lemma 1 facilitates this task: realizing that any tetragonal group K must contain either the cyclic group $\mathsf{4}$ or $\mathsf{\bar{4}}$, every K-orbit of states is, in general, a union of some $\mathsf{4}$-orbits of states or of some of the $\mathsf{\bar{4}}$-orbits. Since the orientations of three fourfold axes are equivalent under $\mathsf{m\bar{3}m}$, one needs to consider only the [001] direction. One deduces the $\mathsf{4_z}$- and $\mathsf{\bar{4}_z}$-orbits from figure 1. Every orbit of any of the tetragonal groups must be among the $\mathsf{4_z}$-orbits $\{1,2,7,8\}$ and $\{3,4,5,6\}$, the $\mathsf{\bar{4}_z}$-orbits $\{1,2,3,4\}$ and $\{5,6,7,8\}$ and the $\mathsf{m\bar{3}m}$-orbit $\{1,2,3,4,5,6,7,8\}$. The stabilizer of both $\mathsf{\bar{4}_z}$-orbits is $\mathsf{\bar{4}3m}$ since each threefold rotation leaves either orbit invariant. Therefore, no principal tetragonal symmetry will contain a rotoinversion $\mathsf{\bar{4}}$. One is left with three possibilities: $\mathsf{4_z}$, $\mathsf{4_zmm}$ and $\mathsf{4_z22}$. As one checks, any

Table 2. Coherent DCs and corresponding driving forces. ($\boldsymbol{T}$—mechanical stress tensor, $\boldsymbol{E}$—intensity of electric field.)

Macroscopic symmetry	Coherent domain configuration	Driving forces
$\mathsf{m}\bar{3}\mathsf{m}$	$\kappa = \langle 1,2,3,4,5,6,7,8\rangle$	
$\bar{4}3\mathsf{m}$	$\lambda_1 = \langle 1,2,3,4\rangle,\ \lambda_2 = \langle 5,6,7,8\rangle$	$\kappa : T_{12}E_3$ [a]
$\bar{3}_{\mathsf{xyz}}2_{\mathsf{x}\bar{\mathsf{y}}}/\mathsf{m}_{\mathsf{x}\bar{\mathsf{y}}}$	$\vartheta_1^{(r)} = \langle 1,5\rangle,\ \vartheta_2^{(r)} = \langle 2,3,4,6,7,8\rangle$	$\kappa : T_{23} = T_{31} = T_{12}$
$\bar{3}_{\mathsf{x}\bar{\mathsf{y}}\bar{\mathsf{z}}}2_{\mathsf{xy}}/\mathsf{m}_{\mathsf{xy}}$	$\vartheta_1^{(x)} = \langle 3,7\rangle,\ \vartheta_2^{(x)} = \langle 1,2,4,5,6,8\rangle$	$\kappa : T_{23} = -T_{31} = -T_{12}$
$\bar{3}_{\bar{\mathsf{x}}\mathsf{y}\bar{\mathsf{z}}}2_{\mathsf{xy}}/\mathsf{m}_{\mathsf{xy}}$	$\vartheta_1^{(y)} = \langle 4,8\rangle,\ \vartheta_2^{(y)} = \langle 1,2,3,5,6,7\rangle$	$\kappa : -T_{23} = T_{31} = -T_{12}$
$\bar{3}_{\bar{\mathsf{x}}\bar{\mathsf{y}}\mathsf{z}}2_{\mathsf{x}\bar{\mathsf{y}}}/\mathsf{m}_{\mathsf{x}\bar{\mathsf{y}}}$	$\vartheta_1^{(z)} = \langle 2,6\rangle,\ \vartheta_2^{(z)} = \langle 1,3,4,5,7,8\rangle$	$\kappa : -T_{23} = -T_{31} = T_{12}$
$4_{\mathsf{x}}\mathsf{mm}$	$\varphi_1^{(x)} = \langle 1,3,6,8\rangle,\ \varphi_2^{(x)} = \langle 2,4,5,7\rangle$	$\kappa : \boldsymbol{E} \parallel [100]$
$4_{\mathsf{y}}\mathsf{mm}$	$\varphi_1^{(y)} = \langle 1,4,6,7\rangle,\ \varphi_2^{(y)} = \langle 2,3,5,8\rangle$	$\kappa : \boldsymbol{E} \parallel [010]$
$4_{\mathsf{z}}\mathsf{mm}$	$\varphi_1^{(z)} = \langle 1,2,7,8\rangle,\ \varphi_2^{(z)} = \langle 3,4,5,6\rangle$	$\kappa : \boldsymbol{E} \parallel [001]$
$\mathsf{m}_{\mathsf{x}}\mathsf{m}_{\mathsf{yz}}\mathsf{m}_{\mathsf{y}\bar{\mathsf{z}}}$	$\mu_1^{(x)} = \langle 1,3,5,7\rangle,\ \mu_2^{(x)} = \langle 2,4,6,8\rangle$	$\kappa : T_{23}$
$\mathsf{m}_{\mathsf{z}\bar{\mathsf{x}}}\mathsf{m}_{\mathsf{y}}\mathsf{m}_{\mathsf{zx}}$	$\mu_1^{(y)} = \langle 1,4,5,8\rangle,\ \mu_2^{(y)} = \langle 2,3,6,7\rangle$	$\kappa : T_{31}$
$\mathsf{m}_{\mathsf{xy}}\mathsf{m}_{\mathsf{x}\bar{\mathsf{y}}}\mathsf{m}_{\mathsf{z}}$	$\mu_1^{(z)} = \langle 1,2,5,6\rangle,\ \mu_2^{(z)} = \langle 3,4,7,8\rangle$	$\kappa : T_{12}$
$3_{\mathsf{xyz}}\mathsf{m}_{\mathsf{x}\bar{\mathsf{y}}}$	$\varpi_1^{(r)} = \langle 1\rangle,\ \varpi_2^{(r)} = \langle 5\rangle$ $\nu_1^{(r)} = \langle 2,3,4\rangle,\ \nu_2^{(r)} = \langle 6,7,8\rangle$	$\vartheta_1^{(r)}: \begin{cases} \boldsymbol{E} \parallel [111], \\ T_{23} = T_{31} = T_{12} \end{cases}$
$3_{\mathsf{x}\bar{\mathsf{y}}\bar{\mathsf{z}}}\mathsf{m}_{\mathsf{xy}}$	$\varpi_1^{(x)} = \langle 3\rangle,\ \varpi_2^{(x)} = \langle 7\rangle$ $\nu_1^{(x)} = \langle 1,2,4\rangle,\ \nu_2^{(x)} = \langle 5,6,8\rangle$	$\vartheta_1^{(x)}: \begin{cases} \boldsymbol{E} \parallel [1\bar{1}\bar{1}], \\ T_{23} = -T_{31} = -T_{12} \end{cases}$
$3_{\bar{\mathsf{x}}\mathsf{y}\bar{\mathsf{z}}}\mathsf{m}_{\mathsf{xy}}$	$\varpi_1^{(y)} = \langle 4\rangle,\ \varpi_2^{(y)} = \langle 8\rangle$ $\nu_1^{(y)} = \langle 1,2,3\rangle,\ \nu_2^{(y)} = \langle 5,6,7\rangle$	$\vartheta_1^{(y)}: \begin{cases} \boldsymbol{E} \parallel [\bar{1}1\bar{1}], \\ -T_{23} = T_{31} = -T_{12} \end{cases}$
$3_{\bar{\mathsf{x}}\bar{\mathsf{y}}\mathsf{z}}\mathsf{m}_{\mathsf{x}\bar{\mathsf{y}}}$	$\varpi_1^{(z)} = \langle 2\rangle,\ \varpi_2^{(z)} = \langle 6\rangle$ $\nu_1^{(z)} = \langle 1,3,4\rangle,\ \nu_2^{(z)} = \langle 5,7,8\rangle$	$\vartheta_1^{(z)}: \begin{cases} \boldsymbol{E} \parallel [\bar{1}\bar{1}1], \\ -T_{23} = -T_{31} = T_{12} \end{cases}$
$2_{\mathsf{x}}\mathsf{m}_{\mathsf{yz}}\mathsf{m}_{\mathsf{y}\bar{\mathsf{z}}}$	$\varsigma_1^{(x)} = \langle 1,3\rangle,\ \varsigma_2^{(x)} = \langle 2,4\rangle,$ $\varsigma_3^{(x)} = \langle 5,7\rangle,\ \varsigma_4^{(x)} = \langle 6,8\rangle$	$\varphi_k^{(x)}, \mu_k^{(x)} : \boldsymbol{E} \parallel [100],\ T_{23}$
$\mathsf{m}_{\mathsf{z}\bar{\mathsf{x}}}2_{\mathsf{y}}\mathsf{m}_{\mathsf{zx}}$	$\varsigma_1^{(y)} = \langle 1,4\rangle,\ \varsigma_2^{(y)} = \langle 2,3\rangle,$ $\varsigma_3^{(y)} = \langle 5,8\rangle,\ \varsigma_4^{(y)} = \langle 6,7\rangle$	$\varphi_k^{(y)}, \mu_k^{(y)} : \boldsymbol{E} \parallel [010],\ T_{31}$
$\mathsf{m}_{\mathsf{xy}}\mathsf{m}_{\mathsf{x}\bar{\mathsf{y}}}2_{\mathsf{z}}$	$\varsigma_1^{(z)} = \langle 1,2\rangle,\ \varsigma_2^{(z)} = \langle 3,4\rangle,$ $\varsigma_3^{(z)} = \langle 5,6\rangle,\ \varsigma_4^{(z)} = \langle 7,8\rangle$	$\varphi_k^{(z)}, \mu_k^{(z)} : \boldsymbol{E} \parallel [001],\ T_{12}$
$\mathsf{m}_{\mathsf{x}}2_{\mathsf{yz}}\mathsf{m}_{\mathsf{y}\bar{\mathsf{z}}}$	$\varrho_1^{(yz)} = \langle 1,7\rangle,\ \varrho_2^{(yz)} = \langle 3,5\rangle$	$\mu_1^{(x)} : \boldsymbol{E} \parallel [011],\ T_{23}$
$\mathsf{m}_{\mathsf{x}}\mathsf{m}_{\mathsf{yz}}2_{\mathsf{y}\bar{\mathsf{z}}}$	$\varrho_1^{(y\bar{z})} = \langle 4,6\rangle,\ \varrho_2^{(y\bar{z})} = \langle 2,8\rangle$	$\mu_2^{(x)} : \boldsymbol{E} \parallel [01\bar{1}],\ -T_{23}$
$\mathsf{m}_{\mathsf{z}\bar{\mathsf{x}}}\mathsf{m}_{\mathsf{y}}2_{\mathsf{zx}}$	$\varrho_1^{(zx)} = \langle 1,8\rangle,\ \varrho_2^{(zx)} = \langle 4,5\rangle$	$\mu_1^{(y)} : \boldsymbol{E} \parallel [101],\ T_{31}$
$2_{\mathsf{z}\bar{\mathsf{x}}}\mathsf{m}_{\mathsf{y}}\mathsf{m}_{\mathsf{zx}}$	$\varrho_1^{(z\bar{x})} = \langle 2,7\rangle,\ \varrho_2^{(z\bar{x})} = \langle 3,6\rangle$	$\mu_2^{(y)} : \boldsymbol{E} \parallel [\bar{1}01],\ -T_{31}$
$2_{\mathsf{xy}}\mathsf{m}_{\mathsf{x}\bar{\mathsf{y}}}\mathsf{m}_{\mathsf{z}}$	$\varrho_1^{(xy)} = \langle 1,6\rangle,\ \varrho_2^{(xy)} = \langle 2,5\rangle$	$\mu_1^{(z)} : \boldsymbol{E} \parallel [110],\ T_{12}$
$\mathsf{m}_{\mathsf{xy}}2_{\mathsf{x}\bar{\mathsf{y}}}\mathsf{m}_{\mathsf{z}}$	$\varrho_1^{(x\bar{y})} = \langle 3,8\rangle,\ \varrho_2^{(x\bar{y})} = \langle 4,7\rangle$	$\mu_2^{(z)} : \boldsymbol{E} \parallel [1\bar{1}0],\ -T_{12}$

[a] Provided that $T_{12} = T_0$ and $E_3 = E_0$ are given by the material properties, and $T_0^2 = f(E_0^2)$.

$2_{\mathsf{x}}2_{\mathsf{y}}2_{\mathsf{z}}$-orbit coincides with some $\bar{4}3\mathsf{m}$-orbit, and each $\mathsf{m}_{\mathsf{x}}\mathsf{m}_{\mathsf{y}}2_{\mathsf{z}}$-orbit is a 4_{z}-orbit as well. One directly gets that $4_{\mathsf{z}}^{\mathsf{c}} = 4_{\mathsf{z}}\mathsf{mm}$. Further, $4_{\mathsf{z}}22 \star 1 \supseteq 4_{\mathsf{z}} \star 1 \cup 2_{\mathsf{x}}2_{\mathsf{y}}2_{\mathsf{z}} \star 1 \supseteq \{3,7\}$ implies that $4_{\mathsf{z}}22 \star 1 = 4_{\mathsf{z}} \star 1 \cup 4_{\mathsf{z}} \star 5 = \{1,\ldots,8\}$, i.e. $(4_{\mathsf{z}}22)^{\mathsf{c}} = \mathsf{m}\bar{3}\mathsf{m}$. One concludes that $4\mathsf{mm}$ is the only tetragonal symmetry that one can engineer in a PZN-PT crystal. For each orientation of a fourfold axis, [100], [010] and [001], there are two coherent DCs and their mixture:

(c1)	$\varphi_1^{(x)} := \langle 1,3,6,8\rangle$	$\varphi_1^{(y)} := \langle 1,4,6,7\rangle$	$\varphi_1^{(z)} := \langle 1,2,7,8\rangle$
(c2)	$\varphi_2^{(x)} := \langle 2,4,5,7\rangle$	$\varphi_2^{(y)} := \langle 2,3,5,8\rangle$	$\varphi_2^{(z)} := \langle 3,4,5,6\rangle$
(m)	$u_1\,\varphi_1^{(x)} \sqcup u_2\,\varphi_2^{(x)}$	$u_1\,\varphi_1^{(y)} \sqcup u_2\,\varphi_2^{(y)}$	$u_1\,\varphi_1^{(z)} \sqcup u_2\,\varphi_2^{(z)}, u_1, u_2 \neq \frac{1}{2}.$

Table 3. Minimal incoherent DCs with non-trivial macroscopic symmetry. Examples of driving forces. ($\boldsymbol{T}$—mechanical stress, $\boldsymbol{E}$—intensity of electric field, $\boldsymbol{e}^{(1)}$ ($e = e^{(1)}_{23} = e^{(1)}_{31} = e^{(1)}_{12}$)—spontaneous deformation of the state $\langle 1\rangle$, $\boldsymbol{P}^{(1)}$ ($P = P^{(1)}_1 = P^{(1)}_2 = P^{(1)}_3$)—spontaneous polarization of $\langle 1\rangle$, $\varepsilon^{(1)}$ ($\varepsilon = \varepsilon^{(1)}_{23} = \varepsilon^{(1)}_{31} = \varepsilon^{(1)}_{12}$)—permittivity of $\langle 1\rangle$.)

Macroscopic symmetry	Coherent domain configurations involved	Minimal incoherent DCs	Driving forces
$2_{x\bar{y}}/m_{x\bar{y}}$	$\vartheta^{(r)}_1 = \langle 1,5\rangle,\ \vartheta^{(z)}_1 = \langle 2,6\rangle,\ \mu^{(z)}_2 = \langle 3,4,7,8\rangle$	$u_1\vartheta^{(r)}_1 \sqcup u_2\vartheta^{(z)}_1,\ u_1 \neq u_2$ $v_1\vartheta^{(a)}_1 \sqcup v_2\mu^{(z)}_2,\ v_2 \neq 2v_1$	$\underline{2_{x\bar{y}}/m_{x\bar{y}}}:\ \ T_{23} = T_{31} \neq T_{12}$ $\mu^{(z)}_1$: $\pm T_{23}$, $\ 0 < \lvert eT_{23}\rvert < \frac{1}{5}eT_{12}$;
$2_{xy}/m_{xy}$	$\vartheta^{(x)}_1 = \langle 3,7\rangle,\ \vartheta^{(y)}_1 = \langle 4,8\rangle,\ \mu^{(z)}_1 = \langle 1,2,5,6\rangle$	$u_1\vartheta^{(x)}_1 \sqcup u_2\vartheta^{(y)}_1,\ u_1 \neq u_2$ $v_1\vartheta^{(b)}_1 \sqcup v_2\mu^{(z)}_1,\ v_2 \neq 2v_1$	$\left.\begin{array}{l}\vartheta^{(z)}_2\text{: } +T_{23}\\ \vartheta^{(r)}_2\text{: } -T_{23}\end{array}\right\}\ \begin{array}{c}3eT_{12} < -\lvert eT_{23}\rvert < \frac{1}{2}eT_{12},\\ -\lvert eT_{23}\rvert \neq eT_{12} < 0\end{array}$
$2_{x\bar{y}}$	$\vartheta^{(r)}_1 = \langle 1,5\rangle,\ \vartheta^{(z)}_1 = \langle 2,6\rangle,\ \varrho^{(x\bar{y})}_1 = \langle 3,8\rangle,\ \varrho^{(x\bar{y})}_2 = \langle 4,7\rangle$	$w_1\vartheta^{(a)}_1 \sqcup w_2\varrho^{(x\bar{y})}_i$	$\underline{2_{x\bar{y}}}:\ T_{23} = T_{31} \neq T_{12},\ E = E_1 = -E_2$
2_{xy}	$\vartheta^{(x)}_1 = \langle 3,7\rangle,\ \vartheta^{(y)}_1 = \langle 4,8\rangle,\ \varrho^{(xy)}_1 = \langle 1,6\rangle,\ \varrho^{(xy)}_2 = \langle 2,5\rangle$	$w_1\vartheta^{(b)}_1 \sqcup w_2\varrho^{(xy)}_i$	$\underbrace{w_1\vartheta^{(r)}_1 \sqcup w_2\varrho^{(x\bar{y})}_1}$
m_z	$\varrho^{(xy)}_1 = \langle 1,6\rangle,\ \varrho^{(xy)}_2 = \langle 2,5\rangle,\ \varrho^{(x\bar{y})}_1 = \langle 3,8\rangle,\ \varrho^{(x\bar{y})}_2 = \langle 4,7\rangle$	$u_1\varrho^{(xy)}_i \sqcup u_2\varrho^{(x\bar{y})}_j,\ u_1 \neq u_2$	1. $2_{x\bar{y}}/m_{x\bar{y}} - v_1\vartheta^{(r)}_1 \sqcup v_2\mu^{(z)}_2,\ v_2 \neq 2v_1$:
$\bar{1}$	$\vartheta^{(r)}_1 = \langle 1,5\rangle,\ \vartheta^{(z)}_1 = \langle 2,6\rangle,\ \vartheta^{(x)}_1 = \langle 3,7\rangle,\ \vartheta^{(y)}_1 = \langle 4,8\rangle$	$t_1\vartheta^{(a)}_1 \sqcup t_2\vartheta^{(b)}_1 \sqcup t_3\vartheta^{(c)}_1$, $t_1 \neq t_2 \neq t_3 \neq t_1$	$W = 2eT_{23} + 2eT_{12} - \varepsilon E^2 > 0$, $(a)\ EP \neq 2W,\ W < EP < 6W,\ W \leqslant eT_{23}$
$m_{x\bar{y}}$	$\varpi^{(r)}_1 = \langle 1\rangle,\ \varpi^{(r)}_2 = \langle 5\rangle,\ \varpi^{(z)}_1 = \langle 2\rangle,\ \varpi^{(z)}_2 = \langle 6\rangle,$ $\varsigma^{(z)}_2 = \langle 3,4\rangle,\ \varsigma^{(z)}_4 = \langle 7,8\rangle$	$u_1\varpi^{(r)}_i \sqcup u_2\varpi^{(z)}_j,\ u_1 \neq u_2$ $v_1\varpi^{(a)}_k \sqcup v_2\varsigma^{(z)}_{2k},\ v_2 \neq 2v_1$ $w_1\varpi^{(a)}_k \sqcup w_2\varsigma^{(z)}_{6-2k}$ $\frac{1}{3}\varpi^{(r)}_i \sqcup \frac{1}{3}\varpi^{(z)}_i \sqcup \frac{1}{3}\varpi^{(a)}_k$	$(b)\ EP = 2W,\ \frac{1}{2}W < eT_{23} < \frac{3}{4}W$ 2. $m_{xy}2_{x\bar{y}}m_z - \bar{v}_1\mu^{(z)}_1 \sqcup \bar{v}_2\varrho^{(x\bar{y})}_1$: $Z = \frac{1}{2}EP - 2eT_{12} + \varepsilon E^2 > 0$, $(a)\ eT_{23} \neq \frac{1}{2}Z,\ \frac{1}{4}Z < eT_{23} < \frac{3}{2}Z,\ 4Z \leqslant EP$
m_{xy}	$\varpi^{(x)}_1 = \langle 3\rangle,\ \varpi^{(x)}_2 = \langle 7\rangle,\ \varpi^{(y)}_1 = \langle 4\rangle,\ \varpi^{(y)}_2 = \langle 8\rangle,$ $\varsigma^{(z)}_1 = \langle 1,2\rangle,\ \varsigma^{(z)}_3 = \langle 5,6\rangle$	$u_1\varpi^{(x)}_i \sqcup u_2\varpi^{(y)}_j,\ u_1 \neq u_2$ $v_1\varpi^{(b)}_k \sqcup v_2\varsigma^{(z)}_{2k-1},\ v_2 \neq 2v_1$ $w_1\varpi^{(b)}_k \sqcup w_2\varsigma^{(z)}_{6-2k-1}$ $\frac{1}{3}\varpi^{(x)}_i \sqcup \frac{1}{3}\varpi^{(y)}_i \sqcup \frac{1}{3}\varpi^{(b)}_k$	$(b)\ eT_{23} = \frac{1}{2}Z,\ 2Z < EP < 3Z$ 3. $2_{x\bar{y}}/m_{x\bar{y}}$ or $m_{xy}2_{x\bar{y}}m_z$ (w_1, w_2—any), $m\bar{3}m - \kappa$ ($w_1 = w_2 = \frac{1}{2}$) : $W = 2eT_{23} = \frac{1}{2}EP = Z$

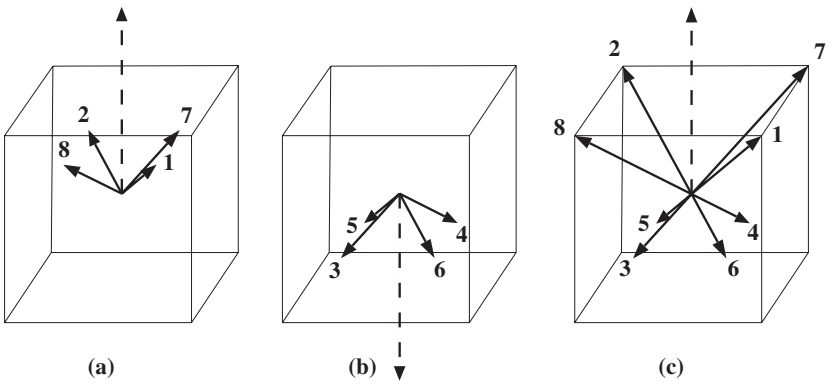

Figure 4. Coherent DCs of the symmetry $\mathsf{H} = 4_z\mathsf{mm}$ and a mixed one: (*a*) $\varphi_1^{(z)} = \langle 1, 2, 7, 8\rangle$; (*b*) $\varphi_2^{(z)} = \langle 3, 4, 5, 6\rangle$; (*c*) $\frac{2}{3}\varphi_1^{(z)} \sqcup \frac{2}{3}\varphi_2^{(z)}$ (scale 3 : 1).

Due to the symmetry 4mm, the effective polarization of the PZN-PT crystal is parallel to the fourfold axis. One can see that the effective polarization $\overline{\boldsymbol{P}}(\varphi_1^{(z)})$ will be oriented up while the polarization $\overline{\boldsymbol{P}}(\varphi_2^{(z)})$ will be oriented down (cf figures 4(*a*), (*b*) in which the scale used is the same as that for other coherent DCs). For a mixed DC $u_1\,\varphi_1^{(z)} \sqcup u_2\,\varphi_2^{(z)}$ (figure 4(*c*)) one obtains the average polarization $\overline{\boldsymbol{P}} = (0, 0, (u_1 - u_2)P)$. Applying a dc bias field along the fourfold axis one can change the values of u_1 and u_2 so that for high enough field only one coherent DC survives. Note that for $u_1 = u_2 = \frac{1}{2}$ a coherent DC of the symmetry $\mathsf{m\bar{3}m}$ results.

5. Determination of possible macroscopic symmetries and of all corresponding DCs of a multidomain crystal

In the preceding section possible tetragonal symmetries and the corresponding DCs of a rhombohedral PZN-PT crystal were found. In order to derive all principal symmetries of the crystal one should proceed in a systematic way. With that aim, we use the one-to-one correspondence between the principal symmetries of such a multidomain crystal and the divisions of the set of all possible states into orbits under H that runs over all subgroups of the prototypic group G (cf section 3). Since every class of equivalent divisions corresponds to at least one class of conjugate subgroups of G (cf lemma 2), one needs to examine one group per class. Moreover, only the supergroups of core F, that gives the minimal symmetry, are to be considered. The algorithm for deriving the principal symmetries is straightforward.

From each class of conjugate subgroups of G, containing the group core F, select a representative group H_j. For each H_j determine all H_j-orbits of states consecutively: by applying all the operations of H_j to the state $\langle 1\rangle$, generate the orbit $\mathsf{H}_j \star i_1 := \mathsf{H}_j \star 1$. If it contains less than n states, another H_j-orbit must exist. Choose a state $\langle i_2\rangle$ from the remaining states and generate the orbit $\mathsf{H}_j \star i_2$. If both the orbits contain less than n states continue in generating further H_j-orbits until no more states are left. For each orbit $\mathsf{H}_j \star i_k$, $k = 1, \ldots, q_j$, find its stabilizer $\mathrm{Stab}_{\mathsf{G}}(\mathsf{H}_j \star i_k)$ among the supergroups of H_j. If $\mathrm{Stab}_{\mathsf{G}}(\mathsf{H}_j \star i_k) = \mathsf{H}_j$ for some k, then $\mathsf{H}_j = \mathsf{H}_j^{\mathsf{c}}$ gives a possible macroscopic symmetry of the crystal. Otherwise, such symmetry equals the intersection $\bigcap_{k=1}^{q_j} \mathrm{Stab}_{\mathsf{G}}(\mathsf{H}_j \star i_k) = \mathsf{H}_j^{\mathsf{c}}$. Note that if a representative H_k is conjugate to the closure $\mathsf{H}_j^{\mathsf{c}}$ in G, i.e. $\mathsf{H}_k = g_{jk}\,\mathsf{H}_j^{\mathsf{c}}\,g_{jk}^{-1}$ (or even $\mathsf{H}_k = \mathsf{H}_j^{\mathsf{c}}$), it need not be dealt with since $\mathsf{H}_k^{\mathsf{c}} = \mathsf{H}_k$. At the end, all principal symmetries are obtained as the closures of certain representatives $\mathsf{H}_{j_1}, \ldots, \mathsf{H}_{j_m}$, i.e. as $\mathsf{H}_{j_1}^{\mathsf{c}}, \ldots, \mathsf{H}_{j_m}^{\mathsf{c}}$.

One should handle the representatives H_j in the following order: first take cyclic groups, and then all the others. In either case, the groups should be processed with the higher precedence given to the lower order of H_j, so that lemma 1 can be used. Consider e.g. the groups $\overline{4}_z 2_x m_{xy}$ and $\overline{4}_z m_x 2_{xy}$ which in addition to the cyclic group $\overline{4}_z$ contain also the group $2_x 2_y 2_z$ and $m_x m_y 2_z$, respectively. According to section 4, $\overline{4}_z \star i = 2_x 2_y 2_z \star i = \overline{4}3m \star i$ and $m_x m_y 2_z \star i = 4_z mm \star i$, $i = 1, 5$. It follows that $(\overline{4}_z 2_x m_{xy})^c = \overline{4}3m$ while $\overline{4}_z m_x 2_{xy} \star 1 = \overline{4}3m \star 1 \cup \overline{4}3m \star 5 = 4_z mm \star 1 \cup 4_z mm \star 5 = \{1, \ldots, 8\}$, i.e. $(\overline{4}_z m_x 2_{xy})^c = m\overline{3}m$.

Two following lemmas and the closure properties (to be given below) can speed up the calculations:

Lemma 3. *Consider a subgroup* H *of the prototypic group* G. *If an* H*-orbit contains all* n *states, i.e.* $\mathsf{G} \star 1 = \mathsf{H} \star 1$, *then for all groups* K, $\mathsf{H} \subset \mathsf{K} \subset \mathsf{G}$, *and for all operations* $g \in \mathsf{G}$, *it holds that* $\mathsf{H}^g \star 1 = \mathsf{K} \star 1 = \mathsf{K}^g \star 1 = \{1, \ldots, n\}$, *where* $\mathsf{H}^g = g\,\mathsf{H}\,g^{-1}$ *is a subgroup of* G *conjugate to* H.

Accordingly, from $\overline{4}_z m_x 2_{xy} \star 1 = \{1, \ldots, 8\}$ one obtains that $\overline{4}_x m_y 2_{yz} \star 1 = \overline{4}_y m_z 2_{zx} \star 1 = 4_z/mmm \star 1 = 4_x/mmm \star 1 = 4_y/mmm \star 1 = \{1, \ldots, 8\}$, i.e. $(\overline{4}m2)^c = (4/mmm)^c = m\overline{3}m$.

Lemma 4. *Suppose that* H *is a normal subgroup in* G, *i.e.* $\mathsf{H}^g = \mathsf{H}$ *for all* $g \in \mathsf{G}$. *Then all* H*-orbits of states form a single* G*-orbit. Take one of them, say* $\mathsf{H} \star i_1$. *Decomposing the group* G *into the left cosets of the stabilizer* $\mathrm{Stab}_{\mathsf{G}}(\mathsf{H} \star i_1)$, $\mathsf{G} = \mathrm{Stab}_{\mathsf{G}}(\mathsf{H} \star i_1) + g' \,\mathrm{Stab}_{\mathsf{G}}(\mathsf{H} \star i_1) + g'' \,\mathrm{Stab}_{\mathsf{G}}(\mathsf{H} \star i_1) + \cdots$, *one obtains the other* H*-orbits by applying the coset representatives* $g', g'', \ldots$, *to* $\mathsf{H} \star i_1$. *Furthermore, the stabilizer of* $\mathsf{H} \star i_1$ *contains the stabilizer of the state* $\langle i_1 \rangle$, *i.e.* $\mathrm{Stab}_{\mathsf{G}}(\mathsf{H} \star i_1) \supseteq \mathsf{F}_{i_1}$. *There are exactly* $[\mathsf{G} : \mathrm{Stab}_{\mathsf{G}}(\mathsf{H} \star i_1)] = |\mathsf{G}|/|\mathrm{Stab}_{\mathsf{G}}(\mathsf{H} \star i_1)|$ H*-orbits, each containing* $|\mathrm{Stab}_{\mathsf{G}}(\mathsf{H} \star i_1)|/|\mathsf{F}_{i_1}|$ *states. If the operations of both groups* H *and* F_{i_1} *generate the whole group* G, *then* $\mathsf{H} \star i_1 = \mathsf{G} \star i_1 = \{1, \ldots, n\}$.

As shown in section 2, under the normal subgroup $\overline{1}$ of $m\overline{3}m$ the set $\{1, \ldots, 8\}$ splits into $[m\overline{3}m : \mathrm{Stab}_{m\overline{3}m}(\overline{1} \star 1)] = |m\overline{3}m|/|\overline{3}_{xyz} 2_{x\overline{y}}/m_{x\overline{y}}| = 4$ orbits, each consisting of $12/6 = 2$ states.

The closure operation (5) has the following properties: for any subgroups $\mathsf{H}_1, \mathsf{H}_2$ of G it holds that

$$(\mathsf{H}_1^c)^c = \mathsf{H}_1^c \supseteq \mathsf{H}_1 \tag{10a}$$

$$(\mathsf{H}_1 \cup \mathsf{H}_2)^c \supseteq \mathsf{H}_1^c \cup \mathsf{H}_2^c \tag{10b}$$

$$(\mathsf{H}_1 \cap \mathsf{H}_2)^c \subseteq \mathsf{H}_1^c \cap \mathsf{H}_2^c \tag{10c}$$

$$\mathsf{H}_1 \supseteq \mathsf{H}_2 \Longrightarrow \mathsf{H}_1^c \supseteq \mathsf{H}_2^c \cup \mathsf{H}_1 \tag{10d}$$

$$\mathsf{H}_1^c \supseteq \mathsf{H}_2 \Longrightarrow \mathsf{H}_1^c \supseteq \mathsf{H}_2^c \tag{10e}$$

$$\mathsf{H}_1 \supseteq \mathsf{H}_2^c \Longrightarrow \mathsf{H}_1^c \supseteq \mathsf{H}_2^c. \tag{10f}$$

The relations $(10d)$–$(10f)$ are special consequences of the primary relations $(10a)$–$(10c)$. We show how these properties can be used. The relation $(10b)$ yields that $(m\overline{3})^c = (\overline{3} \cup 2_z)^c \supseteq \overline{3}^c \cup 2_z^c = \overline{3}2/m \cup m_{xy} m_{x\overline{y}} 2_z = m\overline{3}m$. By $(10d)$ one obtains that $(2_z/m_z)^c \supseteq 2_z^c \cup 2_z/m_z = m_{xy} m_{x\overline{y}} m_z$. Therefore, the symmetries $m\overline{3}$ and $2_z/m_z$ are not principal. The relations $(10e)$, $(10f)$ give an upper or lower bound for the relevant closure: e.g. $(\overline{3}2_{x\overline{y}}/m_{x\overline{y}})^c = \overline{3}2_{x\overline{y}}/m_{x\overline{y}} \supseteq (2_{x\overline{y}}/m_{x\overline{y}})^c$ by $(10e)$ while $(\overline{4}_z 2_x m_{xy})^c \supseteq (2_x 2_y 2_z)^c = \overline{4}3m$ by $(10f)$. One can also check that $\overline{4}_z^c = \overline{4}3m$: first, $\overline{4}_z^c = (\overline{4}_z m_x 2_{xy} \cap \overline{4}_z 2_x m_{xy})^c \subseteq m\overline{3}m \cap \overline{4}3m = \overline{4}3m$ by $(10c)$, and second, $\overline{4}_z^c \supseteq 2_z^c \cup \overline{4}_z = \overline{4}_z 2_x m_{xy}$ by $(10d)$. Finally, $(10e)$ implies that $\overline{4}_z^c \supseteq (\overline{4}_z 2_x m_{xy})^c = \overline{4}3m$.

Applying lemma 4 one finds that each of four normal subgroups of the prototypic group $m\overline{3}m$, $m_x m_y m_z$, 23, $m\overline{3}$ and 432, generates together with the stabilizer $3_{xyz} m_{x\overline{y}}$ of the state $\langle 1 \rangle$ the whole $m\overline{3}m$. The closure of the other normal subgroups of $m\overline{3}m$, $\overline{1}$, $2_x 2_y 2_z$ and $\overline{4}3m$, yields two principal symmetries, $\overline{1} = \overline{1}^c$ and $\overline{4}3m = (2_x 2_y 2_z)^c$. Note that the supergroups of $2_x 2_y 2_z$, $4_z 22$ and $4_z/mmm$, can be ruled out by $(10d)$.

We note that the definition of the closure operation (5) has a useful consequence:

Lemma 5. *The closure of a maximal subgroup* K *of the prototypic point group* G *is either the whole* G, $\mathsf{K}^c = \mathsf{G}$, *or the group itself,* $\mathsf{K}^c = \mathsf{K}$. *In the latter case,* K *is a principal symmetry of the multidomain crystal, and the stabilizers of all* K*-orbits are equal to* K. *A DC of such symmetry is either coherent or mixed but not incoherent.*

As already seen, only two maximal subgroups of $\mathsf{m\bar{3}m}$, $\mathsf{\bar{3}2/m}$ and $\mathsf{\bar{4}3m}$, are principal symmetries of the PZN-PT crystals while $\mathsf{4/mmm}$, $\mathsf{m\bar{3}}$ and $\mathsf{432}$ are not.

Using the suggested hints one derives all possible macroscopic symmetries of multidomain ferroelectric rhombohedral perovskite crystals with a relative ease. The results are given in table 1.

During the derivation, for each principal symmetry $\mathsf{K}_l = \mathsf{H}_{jl}^c$, $l \in \{1, \ldots, m\}$, one must have found all its orbits $\mathsf{K}_l \star i_k$, $k = 1, \ldots, p_l$, and their stabilizers $\mathrm{Stab}_{\mathsf{G}}(\mathsf{K}_l \star i_k)$. Such information enables one to obtain all DCs with a principal symmetry K_l: a simple check of $\mathrm{Stab}_{\mathsf{G}}(\mathsf{K}_l \star i_k) = \mathsf{K}_l$ will yield all *coherent configurations* of the symmetry K_l (if any). Adding to each of them, consecutively one after another, coherent DCs each corresponding to some K_l-orbit, one generates all the *mixed configurations* having the symmetry K_l.

It may happen that $\mathrm{Stab}_{\mathsf{G}}(\mathsf{K}_{l'} \star i_k) \neq \mathsf{K}_{l'}$ $k = 1, \ldots, p_{l'}$, for some principal symmetry $\mathsf{K}_{l'}$. Then any DC of that symmetry will be incoherent. Nevertheless, in a few cases their exist principal symmetries for which both coherent and incoherent DCs exist. An incoherent configuration of the symmetry K_l will appear if two conditions are satisfied:

(1) There are at least two orbits $\mathsf{K}_l \star i_{k_1}, \ldots, \mathsf{K}_l \star i_{k_t}$, $t \geqslant 2$, whose stabilizers differ from K_l, i.e. $\mathrm{Stab}_{\mathsf{G}}(\mathsf{K}_l \star i_{k_1}) \neq \cdots \neq \mathrm{Stab}_{\mathsf{G}}(\mathsf{K}_l \star i_{k_t}) \neq \mathsf{K}_l$.
(2) The intersection of the t stabilizers equals K_l, i.e. $\mathrm{Stab}_{\mathsf{G}}(\mathsf{K}_l \star i_{k_1}) \cap \cdots \cap \mathrm{Stab}_{\mathsf{G}}(\mathsf{K}_l \star i_{k_t}) = \mathsf{K}_l$.

Any *incoherent configuration* of the symmetry K_l can be generated from the minimal incoherent DCs of the same symmetry quite analogously to how mixed DCs are obtained from the coherent ones.

All *minimal incoherent configurations* with the symmetry K_l can be determined step by step. First, from among the orbits $\mathsf{K}_l \star i_k$, $k = 1, \ldots, p_l$, discard all orbits whose stabilizer equals K_l. The remaining ones specify each a coherent DC with the principal symmetry higher than K_l. Denote all these (mutually distinct) symmetries by $\tilde{\mathsf{K}}_1, \ldots, \tilde{\mathsf{K}}_q, \ldots, \tilde{\mathsf{K}}_s$. Second, find all minimal subsets of the set $\{\tilde{\mathsf{K}}_1, \ldots, \tilde{\mathsf{K}}_s\}$ such that the intersection of the groups involved will equal K_l, i.e. if any of the groups within a minimal subset is omitted, then the intersection of the remaining ones will differ from K_l. Then, with each minimal subset, say $\{\tilde{\mathsf{K}}_{q_1}, \ldots, \tilde{\mathsf{K}}_{q_r}\}$, $r \leqslant s$, proceed as follows: for each $\tilde{\mathsf{K}}_{q_j}$, $j = 1, \ldots, r$, select just one of those K_l-orbits whose stabilizer is $\tilde{\mathsf{K}}_{q_j}$. A composition (8) of the corresponding r coherent configurations is a minimal incoherent configuration provided that the respective r weights do not satisfy condition 1 for any supergroup of K_l. Exhausting all combinations of r coherent DCs with the symmetries $\tilde{\mathsf{K}}_{q_1}, \ldots, \tilde{\mathsf{K}}_{q_r}$, one produces all those minimal incoherent configurations in which each coherent DC has a distinct symmetry $\tilde{\mathsf{K}}_{q_j}$. Last, determine all the other minimal incoherent ones (if any) that contain two or more coherent DCs with same symmetry. This is a bit more sophisticated, since every relevant composition of the coherent DCs whose symmetry is one of $\tilde{\mathsf{K}}_1, \ldots, \tilde{\mathsf{K}}_s$ has to be checked separately. In general, if a minimal incoherent DC contains at least two coherent DCs of the symmetry $\tilde{\mathsf{K}}_q$, $q \in \{1, \ldots, s\}$, then after any of them is omitted, one must be able to rewrite a newly formed DC as a composition of coherent DCs corresponding to certain orbits of a principal symmetry $\mathsf{K}_{l'} \supset \mathsf{K}_l$; otherwise the original configuration would not be minimal. Consequently, among the weights of the coherent DCs involved, special relationships should hold, as for the minimal incoherent DC of the symmetry $\mathsf{m}_{\mathsf{x\bar{y}}}$, $\frac{1}{3}\varpi_1^{(r)} \sqcup \frac{1}{3}\varpi_2^{(r)} \sqcup \frac{1}{3}\varpi_2^{(z)}$.

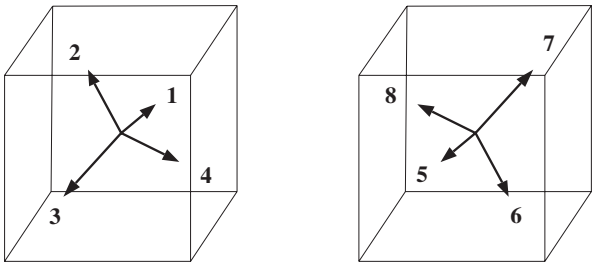

Figure 5. Coherent DCs of the symmetry $\mathsf{H} = \bar{4}3\mathsf{m}$: (*a*) $\lambda_1 = \langle 1, 2, 3, 4\rangle$; (*b*) $\lambda_2 = \langle 5, 6, 7, 8\rangle$.

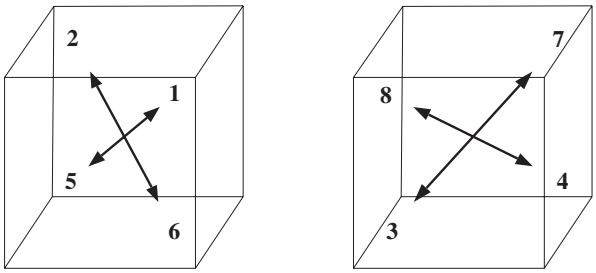

Figure 6. Coherent DCs of the symmetry $\mathsf{H} = \mathsf{m}_{\mathsf{xy}}\mathsf{m}_{\mathsf{x\bar{y}}}\mathsf{m}_{\mathsf{z}}$: (*a*) $\mu_1^{(z)} = \langle 1, 2, 5, 6\rangle$; (*b*) $\mu_2^{(z)} = \langle 3, 4, 7, 8\rangle$.

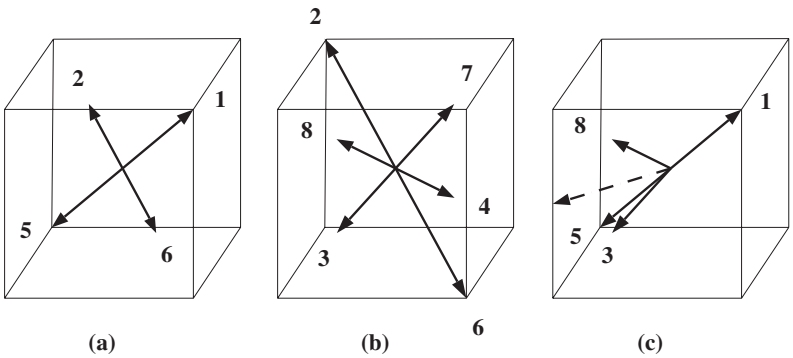

Figure 7. Minimal incoherent DCs of the symmetry $\mathsf{H} = 2_{\mathsf{x\bar{y}}}/\mathsf{m}_{\mathsf{x\bar{y}}}$ (*a*, *b*) and $\mathsf{H} = 2_{\mathsf{x\bar{y}}}$ (*c*): (*a*) $\frac{2}{3}\langle 1, 5\rangle \sqcup \frac{1}{3}\langle 2, 6\rangle$; (*b*) $\frac{1}{2}\langle 2, 6\rangle \sqcup \frac{1}{2}\langle 3, 4, 7, 8\rangle$; (*c*) $\frac{2}{3}\langle 1, 5\rangle \sqcup \frac{1}{3}\langle 3, 8\rangle$ (scale: ((*a*), (*c*)) 3 : 2; (*b*) 2 : 1).

In table 2 we list all the coherent DCs for the PZN-PT crystals with $\mathsf{G} = \mathsf{m}\bar{3}\mathsf{m}$ and $\mathsf{F} = 3\mathsf{m}$. In figures 5 and 6 we represent coherent DCs of the symmetry $\bar{4}3\mathsf{m}$, and $\mathsf{m}_{\mathsf{xy}}\mathsf{m}_{\mathsf{x\bar{y}}}\mathsf{m}_{\mathsf{z}}$, respectively. (We use the same scale for all coherent DCs—cf figures 4(*a*), (*b*).) Table 3 brings together all minimal incoherent configurations for non-equivalent non-trivial principal symmetries; some of these DCs are shown in figures 7 and 8. The superscripts *a*, *b* and *c* in table 3 acquire in the corresponding order two values: *r* or *z*, *x* or *y* and *y* or *z*.

The procedure for finding all DCs with a principal symmetry $\mathsf{K} = \mathsf{K}^{\mathsf{c}}$ illustrates that

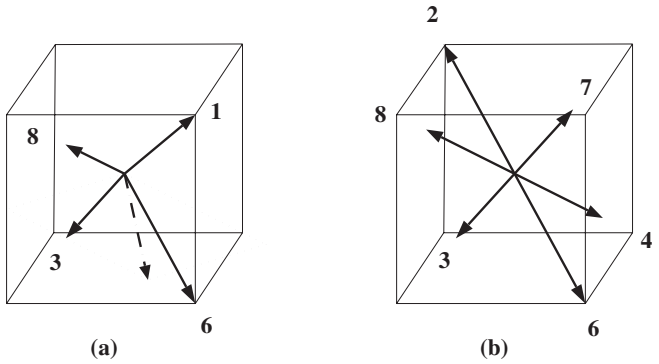

Figure 8. Minimal incoherent DCs of the symmetry $\mathsf{H} = \mathsf{m}_z$ (*a*) and $\mathsf{H} = \bar{1}$ (*b*): (*a*) $\frac{2}{3}\langle 1, 6\rangle \sqcup \frac{1}{3}\langle 3, 8\rangle$; (*b*) $\frac{4}{9}\langle 2, 6\rangle \sqcup \frac{2}{9}\langle 3, 7\rangle \sqcup \frac{1}{3}\langle 4, 8\rangle$ (scale: (*a*) 3 : 2; (*b*) 9 : 4).

coherent configurations are essential building units of multidomain crystals: *any DC of such a crystal exhibiting the symmetry* K *can be expressed as a weighted composition (8) of coherent DCs each corresponding to a* K*-orbit of states.* For example, a DC of a PZN-PT crystal with a symmetry $3\mathsf{m}$ is either trivial—a single domain, or coherent—three states, or else mixed—1 + 1, 1 + 3, . . . states (cf table 2). Assuming that partial volumes of states need not be constant over a $4_z\mathsf{mm}$-orbit, one can infer possible symmetries and DCs of the PZN-PT crystals poled along [001]: $4_z\mathsf{mm}\{4\}$, $\mathsf{m}_{xy}\mathsf{m}_{x\bar{y}}2_z\{2\}$ (coherent), $\mathsf{m}_{xy}\mathsf{m}_{x\bar{y}}2_z\{2+2\}$ (mixed), m_x, $\mathsf{m}_y\{2+2\}$, m_{xy}, $\mathsf{m}_{x\bar{y}}\{1 + 1, 1 + 2, 1 + 1 + 2\}$, and $1\{1 + 1 + 1, 1 + 1 + 1 + 1\}$ (incoherent). In curly braces following symbols we give the number of the states within every coherent DC involved; the sign '+' is used as a separator.

We note that for more than eight states the approach outlined above can be rather extensive, and so we have developed a more efficient algorithm (to appear elsewhere). It is based on the concepts of the twinning group [16] and stabilizing groups [20] that characterize a domain state pair: every stabilizing group as well as the twinning group of a relevant pair yields a principal symmetry and specifies a coherent DC.

6. Driving forces inducing coherent domain configurations in PZN-PT single crystals

While in zero fields the free energy of all possible states is equal, in an applied field these states may have a distinct free energy. If the field is high enough, it will retain only the state(s) of the lowest energy while the other ones will be expelled. Denote by H the maximal subgroup of the prototypic group G which leaves the field(s) invariant. All states present in the DC produced will often constitute a single H-orbit; in such a case the occupied free energy level will be called 'non-degenerate'. However, under certain circumstances the retained states may form several H-orbits, in which case a 'degenerate' free energy level is created: by varying the intensities of applied fields one can suppress all the H-orbits except one.

Consider a subgroup K of G, containing the group H. Suppose that the set of all states contained initially in a multidomain crystal is a union of several K-orbits, and that all states within each K-orbit have equal partial volumes. In other words, assume that the crystal has an engineered DC whose symmetry is at least $\mathsf{K} \supseteq \mathsf{H}$; for $\mathsf{K} = \mathsf{G}$ the crystal will contain all possible states with the same partial volume. Two facts should be taken into account: first, any K-orbit is either an H-orbit or a union of definite H-orbits. Second, any field being invariant under H must have same effect on all states within an arbitrary H-orbit. After an exposure of

the crystal to some field(s) invariant under H, one or more H-orbits will be suppressed and the states within any of the H-orbits left will occupy equal partial volumes. The resulting DC is coherent if only the lowest free energy level is occupied and is non-degenerate. The engineered configuration will be mixed or incoherent if all the states occupy either the lowest free energy level which is degenerate, or more energy levels which may but need not be degenerate. The symmetry of such a 'non-coherent' DC is the intersection $\bigcap_{l\in I} \mathrm{Stab}_{\mathsf{G}}(\mathsf{H}\star i_l)$ (cf (9)), where the orbits $\mathsf{H}\star i_l$, $l \in I$, are all those which survived.

As we will show elsewhere, if no relevant free energy level is degenerate, one of three possibilities will appear, depending on the intersection of the prototypic group G with the symmetry group(s) of the applied field(s): the original free energy level to which all possible domain states belong will

(1) only be shifted—no splitting results; the DCs is not affected;
(2) split into two levels—one can switch between the two corresponding coherent DCs by changing the sign of a relevant field;
(3) split into three or more levels—for each coherent DC there may exist certain intervals to which the values of independent components of the applied field(s) should belong in order that such a DC will be created. In some cases this may be utilized as follows: start with a coherent DC of certain symmetry K, $\mathsf{H}\subset\mathsf{K}\subset\mathsf{G}$, and using a suitable field, split this DC into two coherent ones of the symmetry H as described in (2).

For each coherent DC of the PZN-PT crystals we have derived the field(s) that will induce it. (Detailed information on the method used will be given elsewhere.) The results are presented in table 2: a coherent DC listed in the second column can be produced from the coherent DC given in the third column by means of the field(s) that follow(s). If two fields are indicated, both of them should be applied.

For incoherent DCs the situation is not so simple, as the fourth column of table 3 shows: after the underlined symbol of the principal symmetry, $\underline{2_{x\bar{y}}}/m_{x\bar{y}}$ or $\underline{2_{x\bar{y}}}$, we give the field(s) that can produce a minimal incoherent DC with same symmetry listed in the third column. An initial DC, to which the field(s) should be applied, appears in a row below together with the condition(s) that such field(s) must fulfil. We stress that for any minimal incoherent DC of the symmetry $2_{x\bar{y}}$, three initial DCs exist—incoherent, mixed and coherent; the respective symmetries are $2_{x\bar{y}}/m_{x\bar{y}}$, $m_{xy}2_{x\bar{y}}m_z$ and $m\bar{3}m$. The results for a DC $w_1\vartheta_1^{(r)} \sqcup w_2\varrho_1^{(x\bar{y})}$ are given. We comment on the subcases $(1a)$ and $(2a)$ for which the information presented is only partial: a free energy level, to which all states constituting a coherent DC, say λ_1, belong, is referred to as a λ_1-level. The conditions $(1a)$ apply if the splitting of $\mu_1^{(z)}$-level into $\vartheta_1^{(r)}$- and $\vartheta_1^{(z)}$-levels under a mechanical stress, $T_{23} = T_{31} \neq T_{12} = R$, is more than twice but not more than four times the splitting of the basic κ-level into $\mu_1^{(z)}$- and $\mu_2^{(z)}$-levels due to the stress $T_{12} = R$. The conditions $(2a)$ are valid if the same relation as for the splitting of the $\mu_1^{(z)}$-level into the $\vartheta_1^{(r)}$- and $\vartheta_1^{(z)}$-levels holds for the splitting of $\mu_2^{(z)}$-level into $\varrho_1^{(x\bar{y})}$- and $\varrho_2^{(x\bar{y})}$-levels under an electric field $E_1 = -E_2$. In the other cases the $\vartheta_1^{(r)}$- and $\varrho_1^{(x\bar{y})}$-level degenerate into a single level.

We remark that the concept of a coherent DC is analogous to that of a single-domain state: to each non-trivial coherent DC there exists an equivalent one with the same free energy; these two DCs are related by an operation of the prototypic group G.

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