COLOR GROUPS, LANDAU PHASE TRANSITIONS, AND POSSIBLE SPECIES OF FERROIC CRYSTALS

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Abstract—The theory of crystallographic color groups is shown to provide information which simplifies determining the irreducible representations which satisfy the criteria of the Landau theory of continuous phase transitions and in determining the possible species of nonmagnetic ferroic crystals.

INTRODUCTION: COLOR GROUPS

Generalizations of the classical crystallographic groups have been named color groups\(^1,2\)\). The elements of color groups consist of elements of classical crystallographic groups combined with some additional operator. A general theory of crystallographic color groups has been given by Koptsik and Kotzev\(^1\) and has been the topic of some recent reviews\(^3,4\). Well known special cases of color groups are magnetic groups\(^5\), and spin groups\(^6-10\). These and other color groups have been used in the classification of spin arrangements\(^5\), of crystals with defects\(^2\), and incommensurate crystals\(^11,12\). We consider here the so-called P-type permutational crystallographic color groups\(^1\). Permutational color groups are color groups where each element g of a crystallographic group G is combined with a single permutation p of a permutation group P. All permutational color groups can be derived using a method given by van der Waerden and Burckhardt\(^13\): For each group G and subgroup H' of G one constructs a permutational color group, denoted by \(G(H')\), by combining with each element g the permutation of the left cosets \(gH\) of G under the action of the element g of G.

There is no general agreement on the definition of equivalence classes of these groups\(^4\). We have used a definition of equivalence\(^1,3\) chosen on the basis of physical applications of these groups and tabulated\(^14\) all permutational color point groups. Because of our choice of definition of equivalence, the number of such groups is greater than that tabulated by others\(^1,15,16\). In Table I we list those permutational color point groups \(G(H')\) with \(G=0\) (432).

The application of permutational color groups to the Landau theory of continuous phase transitions is via the irreducible representations contained in the representation \(D_{H'}^g\) associated with each permutational color group \(G(H')\). The representation \(D_{H'}^g\) is the transitive permutation representation of G on the subgroup H' generated by the permutations p combined with each element g in the permutational color group \(G(H')\)\(^14\). In general, the representation \(D_{H'}^g\) is reducible into a sum of irreducible representations of the group G. The irreducible representations contained in \(D_{H'}^g\) have been tabulated for all permutational color point groups\(^14\). In Table I we have listed the number of times each irreducible representation of G is contained in \(D_{H'}^g\), for each of the permutational color point groups \(G(H')\) with \(G=0\).
LANDAU THEORY

The Landau theory of continuous phase transitions\textsuperscript{17} can be applied to transitions in a crystal between phase of symmetry $G$ and $H'$, a subgroup of $G$. The density function of the crystal in the low symmetry phase is written as $\rho_1(r) = \rho_0(r) + \sum_{m} \psi_m(r)$ where $\rho_0$ is the density function of the high symmetry phase and the functions $\psi_m(r)$ are basis functions of irreducible representations $D_G^m$ of the high symmetry phase. For a given high symmetry $G$ and continuous phase transition associated with a specific irreducible representation $D_G^m$, the lower symmetry $H'$ is found by minimizing the thermodynamic potential $\phi(p, T, C_m)$ of the crystal, with the coefficients $C_m$, for the specific $J$, as variational parameters. This minimization determines the density function, above equation, and subsequently the symmetry of the low symmetry phase.

Several group theoretical criteria have been introduced\textsuperscript{17-21} which limit the possible symmetries of the low symmetry phase which can arise in a continuous phase transition. These criteria can be reformulated\textsuperscript{14} on the basis of the theory of permutational color groups and the representations associated with these groups. Some of these criteria are discussed below.

1. Landau Subgroup Criterion: The group $H'$ is a subgroup of the group $G$. All subgroups can be found in a tabulation of the permutational color groups $G(H')$. A complete list of all permutational color point groups is given in reference (14), those with $G=0$ in Table I. A partial list of permutational color space groups has been published\textsuperscript{15,22,23}

2. Subduction Criterion:\textsuperscript{18} The irreducible representation $D_G^m$ associated with a continuous phase transition between phases of symmetry $G$ and $H'$ must be such that $D_G^m$ is restricted to the subgroup $H'$ contains the identity representation of $H'$. This criterion can be reformulated as follows\textsuperscript{14,24}. The irreducible representation $D_G^m$ associated with a continuous phase transition between phases of symmetry $G$ and $H'$ must be contained in the representation $D_G^m$ associated with the permutational color group $G(H')$. The irreducible representations contained in $D_G^m$ associated with all permutational color point groups have been tabulated\textsuperscript{14}, for those groups $G(H')$ with $G=0$ in Table I. Reading across this table, for example, the row alongside $G(H') = 0(C_3)$, one finds that the irreducible representations $D_G^m = \Gamma_1, \Gamma_2, \Gamma_4, \Gamma_5$ satisfy the subduction criterion for continuous phase transitions between $G=0$ and $H'=C_3$. Reading down the table, for example the column under $D_G^m = \Gamma_3$, one finds that this irreducible representation satisfies the subduction criterion for continuous phase transitions between $G=0$ and $H' = G_1, G_2, G_3, G_4, G_5, G_6, G_7, G_8$. Such tables can also be used in the case of equitranslational phase transitions\textsuperscript{14}.

3. Chain Subduction Criterion:\textsuperscript{19,20} The chain subduction criterion further limits the continuous phase transitions associated with an irreducible representation $D_G^m$. A continuous phase transition associated with $D_G^m$ which satisfies the subduction criterion...
for a transition between $G$ and $H'$ may in fact give rise to a phase transition not to $H'$ but to a larger subgroup of $G$. The chain subduction criterion takes this into account. The phase transitions which satisfy the chain subduction criterion are found in the tables of the irreducible representations contained in $D_G^H$ (Table I) and are marked with an asterisk. Reading across Table I, for example the row along $G(H')=O(C_3)$ one finds that only the irreducible representation $D_G^{r_3}$ satisfies the chain subduction criterion for phase transitions between $G=0$ and $H'=C_3$. Reading down Table I, for example the column under $D_G^{r_3}=T_3$, one finds that $r_3$ satisfies the chain subduction criterion only for the transitions between $G=0$ and $H'=D_4$ and $D_4(2,1,1,1,1)$. The low symmetry groups $H'$ which arise in a continuous phase transition associated with an irreducible representation which satisfies the chain subduction criterion coincide, in the case of point groups, with the tabulation given by Janovec, Dvorak and Petzelt and for equitranslational phase transitions with the tabulation of "Maximum Epikernels" of Asher.

4. Tensor Field Criterion: A phase transition in a crystal is a result of a change in some physical property of the crystal. If the physical property is defined by a tensor on the atoms of the crystal, then the tensor field criterion states that the irreducible representation $D_G^H$ associated with the phase transition between $G$ and $H'$ must be contained in the tensor field representation $D_G^{TM}$. $D_G^{TM}=D_G 	imes D_G^{PERM}$. $D_G$ is the representation of the physical property tensor and $D_G^{PERM}$ the permutation representation which describes how the atoms permute under elements of $G$.

It has been shown that the representations $D_G^{PERM}$ are related to the representation $D_G^H$ associated with permutational color groups $G(H')$. $D_G^H$ contains in the second equation, above, for tensor representations $D_G = D_V$, the polar vector representation, $D_A$, the axial vector representation, $D_B = D_A$, and $D_B^{12}$, and $D_G^{PERM} = D_G^H$ for all permutational color point groups $G(H')$ have been tabulated. Table II lists such a tabulation for the group $G(H') = O(O)$. Additional physical applications of these tables are considered elsewhere.

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<th>$r_1$</th>
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<th>$r_4$</th>
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</table>

The possible species of nonmagnetic ferroic crystals can be determined from the tables of irreducible representations contained in the representation $D_G^H$ associated with the permutational color point groups $G(H')$. Consider a phase transition between a prototypic phase of prototypic point group symmetry $G$ and a ferroic phase with $H'$ as the ferroic point group of one of the orientation states. Let the orientation state be characterized by a physical property tensor which transforms under $G$, in the simplest case, as a single irreducible representation $D_G$. Full or partial ferroic species $G(H')$ are determined by the chain-subduction criterion as follows: (1) If the irreducible representation $D_G$ is contained in $D_G^H$, and the number of times appears with an asterisk, $G(H')$ is a full ferroic species; (2) If $D_G$ is contained in $D_G^H$, and the number of times appears without an asterisk, $G(H')$ is a partial ferroic species.
For example, electric polarization transforms as the polar vector representation \( D^{u}_4 \). For the point group \( C=0 \), from Table II, \( D^{u}_4=\Gamma_4 \). From the column under \( \Gamma_4 \) in Table I, one finds that \( OFC_4 \), \( OFC_6 \), \( OFC_9 \), and \( OFC_4 \) are full ferroelectric species, and \( OFC_2 \) is a partial ferroelectric specie.

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