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Ferroelectric Transitions in Diperiodic Systems

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Ferroelectric phase transitions in the 80 diperiodic space groups are discussed. The lower symmetry space groups arise from single multicomponent order parameters in systems of diperiodic symmetry. We obtain and list ferroelectric-nonferroelastic transitions and ferroelastoelectric transitions. These transitions are obtained by imposing appropriate restrictions on the point groups for adjacent phases. We also indicate those transitions which are allowed to be continuous within the Landau theory.

§1. Introduction

The structure of two-dimensional (2D) systems and the transformations they undergo is of current theoretical and experimental interest. Theoretically, 2D systems are intriguing because they often have a variety of characteristics which distinguish their description from that of three-dimensional (3D) systems. For example, renormalization group (RG) techniques in 3D show that anisotropic fourth order terms in the Landau-Ginsburg-Wilson (LGW) Hamiltonian are not relevant for order parameters with two (n=2) or three (n=3) components. We thus always obtain isotropic (Heisenberg) critical fluctuations.[1] However, for 2D systems, anisotropic fourth order terms may be relevant[2] for $n=2$, 3.

The Landau theory is a conceptually straightforward yet powerful description of continuous transitions. It has been widely used in 3D systems to obtain possible symmetry changes. However, only within the last few years has it been systematically applied to the description of transitions in 2D systems. Several authors have recently considered transitions in such systems and using the Landau theory they have obtained a listing of lower symmetry phases[3,4] as well as the corresponding LGW forms.[5]

When describing transitions in a surface system the symmetry will be that of the surface and the substrate (or semi-infinite bulk). The symmetry group of the system as well as its new phase is then one of the 17 2D space groups. However, if a layer is weakly coupled to the bulk, or isolated, then the layer can have more symmetry than included in the possibiliites given by these 17 space groups. The symmetry groups appropriate for free layers are the 80 diperiodic space groups and have been listed by Wood.[6] Of course the diperiodics also include the 17 2D space groups.

We have recently obtained the complete listing of possible lower symmetry subgroups (for $\boldsymbol{k}$ points of symmetry) in the 230 3D space groups,[7] the 17 2D space group,[8] and the 80 diperiodic space groups.[9] Here, for the diperiodics, we will list those transitions which are ferroelectric transitions and will indicate those which can be continuous. We will distinguish ferroelectic-nonferroelastic transitions from ferroelastoelectric transitions. Below we review our method of obtaining symmetry subgroups and then consider the restriction of point group changes for ferroelectric transitions.

§2. Procedure for Distinguishing Ferroelectric Transitions

The Landau theory for continuous transitions consists of minimizing the fourth order thermodynamic potential $\Phi(\boldsymbol{\eta})$ as a function of the order parameter $\boldsymbol{\eta}$. $\boldsymbol{\eta}$ is an n-component vector in the carrier space E of an active irreducible representation (irrep) D(g) of the elements g in the high symmetry space group G. In 3D the restriction that the irrep be active means that it satisfies the Landau[10] and the Lifshitz[11] conditions. In 2D, irreps that do not satisfy the Landau condition are also considered since there is evidence[2,12,13] that a transition may violate this condition but still be continuous when fluctuations are included. The space group of the lower symmetry phase is obtained as the set of transformations which leave the density function $\delta\rho(\boldsymbol{r})$ invariant. As is usually done in the Landau theory $\delta\rho(\boldsymbol{r})$ is expressed as a linear expansion $\delta\rho(\boldsymbol{r})=\Sigma_i\eta_i\phi_i(\boldsymbol{r})$ in terms of the basis functions $\phi_i(\boldsymbol{r})$ of the irrep (of G) being considered. An isotropy subgroup is selected by obtaining the largest subgroup G′ of G leaving $\delta\rho(\boldsymbol{r})$ fixed. Group theoretically this means that G′ must satisfy the subduction criterion[14] and the chain criterion.[15,16] These conditions can also be used as sufficient conditions to determine isotropy subgroups.

The subgroups corresponding to the minimization of the fourth order potential $\Phi(\boldsymbol{\eta})$ will determine those isotropy subgroups G′ of G which may correspond to continuous transitions. Since minimization of a general $\Phi(\boldsymbol{\eta})$ (not just a fourth order expansion) will yield a solution $\boldsymbol{\eta}_{\min}$, the isotropy subgroup which leaves $\boldsymbol{\eta}_{\min}$ fixed will be distinguished. *The isotropy group listing thus yields both continuous and discontinuous transitions obtained as minima of a general potential function of a single, n-component, order parameter* $\boldsymbol{\eta}$.

Recently we discussed[17] a systematic method for obtaining isotropy subgroups of a space group G. The systematic procedure for selecting such subgroups is straightforward. First we look for the largest translation subgroup $T' \subset T$ which satisfies the condition

$$\sum_{t' \varepsilon T'} \frac{e^{-i\boldsymbol{k}_\sigma \cdot \boldsymbol{t}'}}{|T'|}=1.$$

Here σ labels an arm of the star. Sublattices T′ for other isotropy subgroups are obtained by allowing successively more arms of the star to play a role and imposing the above condition simultaneously for all arms being considered. Second, coset representatives of T′ in G′ are selected by requiring (a) that their point group parts leave the lattice unchanged and (b) that they, together with the translations, form a group. The fractional parts of the coset representatives are of the form $\{s_i|\tau_i+t\}$. Here τ_i is the fractional part with respect to G and t can be a primitive translation of G but is a fractional with respect to T′. Third, the chain criterion is applied to the listing of subgroups obtained by this method, i.e., we keep only the largest subgroups for each subduction frequency.

Toledano and Toledano[18] have indicated the point group changes consistent with ferroelectric-nonferroelastic transitions. We impose those point group changes. Also for $\boldsymbol{k}\neq 0$ we impose $n\neq 1$.

They have also indicated point group changes consistent with secondary and higher order ferroics.[19] We will restrict our attention here to the detailed results of ferroelastoelectric transitions and impose the point group changes as given in ref. 19. Again for $\boldsymbol{k}\neq 0$ we require $n\neq 1$.

§3. Results and Discussion

In Table I we list the allowed symmetry changes for ferroelectric-nonferroelastic phase transitions in the diperiodic space groups. As indicated in §2 we want to also list results for irreps that fail the Landau condition. In column 1 we list the paraelectric diperiodic space group together with the number used by Wood.[6] Each diperiodic is related to one of the 3D space groups. We

Table I. Ferroelectric-nonferroelastic transitions in the diperiodic space groups. The space group is given with notation (and number) of ref. 6. The labeling of irreps is that of ref. 20.

PSG 1	2	3	4	5	6	7	8	FNFSG 9
46 P2/n 2_1/m 2_1/m	S1	2	0	1	2	1	*	34 C2mm
	S2	2	0	1	2	1	*	34 C2mm
52 P4/n	M2	2	0	1	2	1	*	49 P4
54 P4$2_1$2	M5	2	0	1	2	1	*	49 P4
64 P4/n 2_1/m 2/m	M3	2	0	1	2	1	*	55 P4mm
	M4	2	0	1	2	1	*	56 P4bm
66 P$\bar{3}$	M1−	3	0	3	4	1	*	65 P3
67 P312	M2	3	0	3	4	1	*	65 P3
68 P321	K2⊕K2*	2	0	1	3	2	*	65 P3
	M2	3	0	3	4	1	*	65 P3
71 P$\bar{3}$12/m	M2−	3	0	3	4	1	*	70 P31m
72 P$\bar{3}$ 2/m 1	K2	2	0	2	3	1	*	70 P31m
				2	3	2		65 P3
	M2−	3	0	3	4	1	*	69 P3ml
74 P$\bar{6}$	K2⊕K2*	2	0	1	3	2	*	65 P3
	K4⊕K4*	2	0	1	3	2	*	65 P3
	K6⊕K6*	2	0	1	3	2	*	65 P3
	M2	3	0	3	4	1	*	65 P3
75 P6/m	K2	2	0	2	3	1	*	73 P6
				2	3	2		65 P3
	M1−	3	0	3	4	1	*	73 P6
76 P622	K2	2	0	2	3	1	*	73 P6
				2	3	2		65 P3
	M2	3	0	3	4	1	*	73 P6
78 P$\bar{6}$m2	K2	2	0	2	3	1	*	70 P31m
				2	3	2		65 P3
	K4	2	0	2	3	1	*	70 P31m
				2	3	2		65 P3
	K6	2	0	2	3	1	*	70 P31m
				2	3	2		65 P3
	M3	3	0	3	4	1	*	69 P3ml
79 P$\bar{6}$2m	K3⊕K3*	2	0	1	3	2	*	69 P3ml
	M3	3	0	3	4	1	*	70 P31m
80 P6/m 2/m 2/m	K3	2	0	2	3	1	*	77 P6mm
				2	3	2		69 P3ml
	M2−	3	0	3	4	1	*	77 P6mm

Table II. ferroelastoelectric transitions in the diperiodic space groups. The space group is given with notation (and number) of ref. 6. The labeling of irreps is that of ref. 20.

PSG 1	2	3	4	5	6	7	8	FEESG 9
37 P2/m 2/m 2/m	Γ1−	1	0	1	1	1	*	19 P222
38 P2/a 2/m 2/a	Γ1−	1	0	1	1	1	*	19 P222
39 P2/n 2/b 2/a	Γ1−	1	0	1	1	1	*	19 P222
40 P2/m 2_1/m 2/a	Γ1−	1	0	1	1	1	*	20 P22$2_1$
41 P2/a 2_1/m 2/m	Γ1−	1	0	1	1	1	*	20 P22$2_1$
42 P2/n 2/m 2_1/a	Γ1−	1	0	1	1	1	*	20 P22$2_1$
43 P2/a 2/b 2_1/a	Γ1−	1	0	1	1	1	*	20 P22$2_1$
44 P2/m 2_1/b 2_1/a	Γ1−	1	0	1	1	1	*	21 P2$2_1$$2_1$
45 P2/a 2_1/b 2_1/m	Γ1−	1	0	1	1	1	*	21 P2$2_1$$2_1$
46 P2/n 2_1/m 2_1/m	Γ1−	1	0	1	1	1	*	21 P2$2_1$$2_1$
47 C2/m 2/m 2/m	Γ1−	1	0	1	1	1	*	22 C222
48 C2/a 2/m 2/m	Γ1−	1	0	1	1	1	*	22 C222
51 P4/m	Γ2−	1	0	1	1	1	*	50 P$\bar{4}$
52 P4/n	Γ2−	1	0	1	1	1	*	50 P$\bar{4}$
61 P4/m 2/m 2/m	Γ1−	1	0	1	1	1	*	53 P422
	Γ2−	1	0	1	1	1	*	57 P$\bar{4}$2m
	Γ4−	1	0	1	1	1	*	59 P$\bar{4}$m2
62 P4/n 2/b 2/m	Γ1−	1	0	1	1	1	*	53 P422
	Γ2−	1	0	1	1	1	*	57 P$\bar{4}$2m
	Γ4−	1	0	1	1	1	*	60 P$\bar{4}$b2
	M1	2	0	1	2	1	*	53 P422
	M2	2	0	1	2	1	*	54 P4$2_1$2
63 P4/m 2_1/b 2/m	Γ1−	1	0	1	1	1	*	54 P4$2_1$2
	Γ2−	1	0	1	1	1	*	58 P$\bar{4}$$2_1$m
	Γ4−	1	0	1	1	1	*	60 P$\bar{4}$b2
64 P4/n 2_1/m 2/m	Γ1−	1	0	1	1	1	*	54 P4$2_1$2
	Γ2−	1	0	1	1	1	*	58 P$\bar{4}$$2_1$m
	Γ4−	1	0	1	1	1	*	59 P$\bar{4}$m2
	M1	2	0	1	2	1	*	58 P$\bar{4}$$2_1$m
	M2	2	0	1	2	1	*	57 P$\bar{4}$2m
71 P$\bar{3}$12/m	Γ1−	1	0	1	1	1	*	67 P312
	M1−	3	0	3	4	1	*	67 P312
72 P$\bar{3}$ 2/m 1	Γ1−	1	0	1	1	1	*	68 P321
	K1	2	1	2	3	2		67 P312
	M1−	3	0	3	4	1	*	68 P321
75 P6/m	Γ2−	1	0	1	1	1	*	74 P$\bar{6}$
	K1	2	1	2	3	2		74 P$\bar{6}$
	M2−	3	0	3	4	1	*	74 P$\bar{6}$
77 P6mm	Γ2	1	0	1	1	1	*	73 P6
	K2	2	0	2	3	1	*	73 P6
	M2	3	0	3	4	1	*	73 P6
78 P$\bar{6}$m2	Γ2	1	0	1	1	1	*	74 P$\bar{6}$
	K1	2	1	2	3	2		74 P$\bar{6}$
	K3	2	1	2	3	2		74 P$\bar{6}$
	K5	2	1	2	3	2		74 P$\bar{6}$
	M2	3	0	3	4	1	*	74 P$\bar{6}$
79 P$\bar{6}$2m	Γ4	1	0	1	1	1	*	74 P$\bar{6}$
	K4⊕K4*	2	0	1	3	2	*	74 P$\bar{6}$
	M4	3	0	3	4	1	*	74 P6
80 P6/m 2/m 2/m	Γ1−	1	0	1	1	1	*	76 P622
	Γ3−	1	0	1	1	1	*	79 P$\bar{6}$2m
	Γ4−	1	0	1	1	1	*	78 P$\bar{6}$m2
	K1	2	1	2	3	2		78 P$\bar{6}$m2
	K2	2	0	2	3	1	*	76 P622
				2	3	1	*	79 P$\bar{6}$2m
	K4	2	0	2	3	2		74 P$\bar{6}$
	M1−	3	0	3	4	1	*	76 P622
	M3−	3	0	3	4	1	*	79 P$\bar{6}$2m
	M4−	3	0	3	4	1	*	78 P$\bar{6}$m2

fbllow the correspondence and orientation given by Wood.[6] Thus in column 2 we give the Brillouin zone point of symmetry with the $\boldsymbol{k}$ point being labeled as in ref. 20 for the three dimensional space groups. In columns 3 thru 5 we give the dimension of the irrep, the Landau frequency, and the number of arms contributing. Column 6 gives the size of the unit cell change. Column 7 gives the subduction frequency. Column 8 indicates by an asterisk (*) that the subgroup is maximal. Column 9 lists the isotropy subgroup.

We have not included ferroelectric-nonferroelastic transitions corresponding to $\boldsymbol{k}=0$. These can be obtained from previously published results for equitranslational transitions, *e.g.* the listings by Janovec *et al.*[21] All such transitions arise from one dimensional $\boldsymbol{k}=0$ irreps. By appropriately restricting the point group changes and using the listing of diperiodics by Wood[6] these transitions can easily be obtained.

In Table II we list the allowed symmetry changes for ferroelastoelectric transitions. The columns are ordered as in Table I.

To determine which transitions in Tables I and II are continuous within the Landau theory the fourth order potential expansion needs to be minimized. As can be seen from the above tables all irreps considered are of one, two, or three dimensions. Within the Landau theory those irreps which fail the Landau condition (Landau frequency not equal to zero) cannot give rise to continuous transitions along a line in P, T variables. The remaining irreps have images (the set of representation matrices) which are isomorphic to the Ising, C_{4v}, C_6, C_{6v}, T_h, O, and O_h images. (See Gufan[22] for descriptions of each image and the associated invariant potential). For the listing of transitions in Tables I and II those transitions which fail the Landau condition or have subduction frequency different from i(g) $=1$ are not continuous within the Landau theory. From the image of the irrep, we used a method described by Kim[23] to determine the minima of the Landau potential (see ref. 9 for details of the process applied to the C_{4v} image.) Our results are consistent with those first published by Gufan.[22]

Consideration of fluctuations (*e.g.* RG methods) often change the continuous vs. discontinuous nature of the transition. As a result the continuous nature and the critical properties of the transition obtained by our analysis is not expected to be reliable close to the transition.

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