Structural phase transitions in crystals of $R\bar{3}c$ symmetry

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A systematic classification of phase transitions corresponding to a variety of points in the Brillouin zone is made for the $R\bar{3}c(D_{3d}^6)$ structure. The Landau group-theoretical description of continuous transitions as formulated by Birman and Jarić is the framework for the classification. Only order parameters corresponding to the $\vec{\Gamma}$ and $\vec{F}$ points satisfy the necessary conditions. The resulting subgroups are indicated together with their translational subgroups as expressed in terms of the original trigonal primitive translations. Nonprimitive as well as primitive subgroups are included.

I. INTRODUCTION

The classification of transitions taking place consistent with the Landau description of second-order phase transitions has been approached in a more systematic way in the last few years. Using the Landau theory in its classical form the possible symmetry changes compatible with the Landau conditions were classified in classes D_4 and C_{4h},[1] in a selection of D_{2d} structures,[2] and in $T^4(P2_13)$ structures.[3] Birman[4] introduced a set of symmetry conditions which were to replace the "lengthy and . . . unnecessary process" of minimization contained within this classical formulation. The equivalence of the set of symmetry conditions to the classical formulation raised some controversy[5] which led to multiple stages of strengthening of the symmetry conditions.[6] Only recently Jarić[7] has proven the equivalence of the chain criterion to the restriction on the subgroup which arises in the classical formulation from the invariance of the linear form of the order parameter. As a result, the usage of the complete set of symmetry conditions has been placed on a footing equal to that of the classical formulation. The Birman-Jarić set of symmetry conditions was used to classify the phase transitions resulting from an $O_h^3(Pm3n)$ structure.[8] That work was later clarified with the additional consideration of nonprimitive lower-symmetry structures.[9]

There are several rhombohedral structures in which phase transitions have been observed or indicated.[10–12] In the references cited the continuous or discontinuous nature obtained from the Landau description played a significant role. The transition characteristic either pointed to the need for greater experimental precession or was motivational in the modeling of the transition. Recently the Landau formalism was used to describe the transition of the calcite – $CaCO_3$(II) transition.[13] Calcite is a $R\bar{3}c(D_{3d}^6)$ structure which can go continuously to a $P2_1/c(C_{2h}^5)$ structure by a zone-boundary wave vector. The Landau formalism was also used to classify invariant contributions to the free energy in calcite and resulted in a formalism similar to that of the stressed perovkite structures.[14]

In the present paper a systematic classification of transitions corresponding to a variety of points of the Brillouin zone is reported for the $R\bar{3}c(D_{3d}^6)$ structure. The Birman-Jarić set of symmetry conditions is used. Lower-symmetry space groups consistent with the symmetry conditions are indicated and two transitions are given as examples of the resulting classification.

II. METHOD

The context in which the question of phase transitions and their nature is considered is within the Landau formalism. The formalism is a phenomenological thermodynamic description which neglects fluctuations. The classical formulation has been reviewed[15] in many places and will not be reviewed here.

The equivalent set of Birman-Jarić conditions selecting possible continuous transitions are to be applied to a single irreducible representation (irrep.) and take the following form:

(A) G_1 is a subgroup of G^0.

(B) The symmetrized triple Kronecker product of the (irrep.) D of G^0 shall not contain the identity representation Γ_1^+ of G^0, i.e.,

$$\{[D]^3|\Gamma_1^+(G^0)\}=0\ .$$

(C) The antisymmetrized double Kronecker product of D shall not contain the representation of a polar vector, i.e.,

$$[\{D\}^2|V(G^0)]=0\ .$$

(D) D of G^0 must subduce into Γ_1^+ of G_1 (subduction criterion).

(D′) If $G^0 \supset G_1 \supset G_1'$, and D of G^0 subduces into $\Gamma_1^\dagger$ of G_1, $i(G_1)$ times, and D of G^0 subduces into $\Gamma_1^\dagger$ of G_1', $i(G_1')=i(G_1)$ times, then the transition $G_0 \rightarrow G_1'$ is eliminated as being second order (chain criterion).

(E) D of G^0 corresponds to a physical tensor field.

If an irrep. does not satisfy condition (B) then we predict a first-order transition arising from a third-order invariant term in the free-energy expansion. Condition (C) expresses the stability against spatial inhomogeneities of the less symmetric phase. A deficiency in the derivation of this condition has been pointed out.[16] Goshen *et al.*[17] subsequently divided continuous transitions into two categories relative to condition (C): (i) The occurring ordered structure arises from a $\vec{k}$ vector which is not "due to symmetry," i.e., it need not satisfy condition (C). The transition may then give rise to a spatially inhomogeneous structure. (ii) The symmetry breaking is "due to symmetry," i.e., it necessarily satisfies condition (C). The transition then gives rise to a spatially homogeneous crystalline phase. In addition Dvorak[18] and Bak *et al.*[19] have indicated that a transition to a homogeneous state contradicting condition (C) must then be first order. Therefore in order that the new phase be achievable by a continuous transition and be homogeneous, it is necessary that condition (C) be satisfied. In the present work it is assumed that (C) is strictly valid.

In the application of the above conditions we will work directly from the symmetry of the order parameter which is taken as spanning an irrep. of G^0. Thus condition (E) is assumed satisfied. The process of classification is to first select an irrep. $D^{(*\vec{k},m)}$ of G^0 and to apply condition (B). Only those irreps. satisfying (B) give transitions consistent with our classification. Condition (C) is next applied and only those irreps. are kept which also satisfy this condition. From a $D^{(*\vec{k},m)}$ which has satisfied both (B) and (C) we look for subgroups of G^0 which are subduced from $D^{(*\vec{k},m)}$ with subduction frequency $i(G_1)\geq 1$. The subduction condition imposes restrictions on the set of possible translational subgroups as well as imposing point-group compatibility restrictions. Such a subgroup satisfies conditions (A) and (D). The chain criterion is then applied to the resulting set of subgroups. Those subgroups which remain are then compared for compatibility with the space groups of Ref. 20 by translation and/or rotation of origin.

III. APPLICATION TO $R\bar{3}c$ STRUCTURE

The prototypic symmetry group G^0 for consideration here is $R\bar{3}c\,(D_{3d}^6)$. $R\bar{3}c$ is a nonsymmorphic space group so appropriate consideration must be given to nonprimitive contributions from the coset representatives as the irrep. is constructed. The coset sum with respect to the translations (T) of $R\bar{3}c$ takes the form

$$G^0(R\bar{3}c)=\sum_{i=1}^{6}\{R_i|000\}T+\sum_{i=7}^{12}\{R_i|\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\}T\ .$$

The numbering of point-group operations R_i correspond to the ordering of the International Tables. We take the forms

$$\vec{t}_1=-a\hat{j}+c\hat{k}\ ,$$
$$\vec{t}_2=(a\sqrt{3}/2)\hat{i}+(a/2)\hat{j}+c\hat{k}\ ,$$
$$\vec{t}_3=-(a\sqrt{3}/2)\hat{i}+(a/2)\hat{j}+c\hat{k}$$

for the primitive translation vectors and

$$\vec{g}_1=2\pi[-(2/3a)\hat{k}_y+(1/3c)\hat{k}_z]\ ,$$
$$\vec{g}_2=2\pi[(1/\sqrt{3}a)\hat{k}_x+(1/2a)\hat{k}_y+(1/3c)\hat{k}_z]\ ,$$
$$\vec{g}_3=2\pi[-1/\sqrt{3}a)\hat{k}_x+(1/3a)\hat{k}_y+(1/3c)\hat{k}_z]$$

are the resulting forms for the reciprocal-lattice vectors.

To construct representations of $R\bar{3}c$ we must have a specific $\vec{k}$ vector in mind. Use is made of the labeling of symmetry points in the Brillouin zone as indicated by Bradley and Cracknell.[21] As indicated in Ref. 22, condition (C) disallows all $\vec{k}$ vectors whose point group does not contain a central point. Considerations then reduce to the points $\vec{\Gamma}=(000)$, $\vec{Z}=(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, $\vec{L}=(0,\frac{1}{2},0)$, and $\vec{F}=(0,\frac{1}{2},\frac{1}{2})$.

Corresponding to the $\vec{\Gamma}$ point there are six irreducible representations of $R\bar{3}c$. For the $\vec{\Gamma}$ point $\vec{k}=0$ so considerations reduce to checking conditions (A)–(D′) on irreps. of that point group $D_{3d}(\bar{3}M)$. All of the representations $D^{(\vec{0},m)}$ satisfy (C) and representations $D^{(\vec{0},m)}$, $m=2,3,4,6$ satisfy condition (B). (The labeling of the representations are as given in Bradley and Cracknell.) Thus there are four representations arising from $\vec{\Gamma}$ to which conditions (A), (D), and (D′) must be applied.

Corresponding to $\vec{Z}$ there are two physically irreducible representations of $R\bar{3}c$. Since $R\bar{3}c$ is nonsymmorphic and $\vec{Z}$ a zone-boundary point both a translation and a coset condition must be satisfied for conditions (B) and (C). The method is shown for the $\vec{F}$ point in Ref. 11. Both irreps. are found to satisfy condition (B) while neither satisfies the antisymmetric square condition (C). Thus no representations corresponding to the $\vec{Z}$ point can lead to transitions consistent with our classification.

Corresponding to $\vec{L}$ there is one irrep. of $R\bar{3}c$. It satisfies the symmetric cube condition (B) but does not satisfy the antisymmetric square condition (C). Therefore no representation for $\vec{L}$ can give rise to a continuous (or nearly continuous) transition.

Corresponding to the $\vec{F}$ point there are four representations of $R\bar{3}c$. All four representations satisfy condition (C) while irreps. $D^{(*\vec{F},1)}$, $D^{(*\vec{F},2)}$,

TABLE I. Basis vectors for the translational subgroups arising from an $R\bar{3}c$ structure. For the nonprimitive subgroups the equivalent translation vectors are also given. All vectors and cell volumes are given in terms of the original trigonal primitive translations.

Irrep.	Translational subgroup	Basis: $\vec{e}_1', \vec{e}_2', \vec{e}_3'$	Equivalent translations	Unit-cell volume
$\vec{\Gamma}$	a (trigonal)	(1,0,0);(0,1,0);(0,0,1)	...	1
	b (monoclinic) $\sim a$	(1,0,1);(1,0,−1);(1,1,1)	(1,0,0)	2
$\vec{F}$	a (monoclinic)	(0,0,1);(−1,1,0);(−1,−1,1)	...	2
	b (trigonal)	(1,−1,1);(1,1,−1);(−1,1,1)	...	4
	c (monoclinic) $\sim b$	(0,0,2);(2,−2,0);(1,1,1)	(1,−1,1)	8

and $D^{(*\vec{F},4)}$ satisfy condition (B). There are then three irreps. to which conditions (A), (D), and (D′) must be applied.

The subgroup condition (A) and subduction conditions (D) and (D′) are contained within the following group-theoretical character sum;

$$\frac{1}{|G_1|}\sum_{\vec{t}'\in G_1}\sum_{\substack{g'\in \text{ cosets of}\\ T' \text{ in } G_1}}\chi^{(*\vec{k},m)}(g'\vec{t}')=n\equiv i(G_1)\ ,\quad (1)$$

where n is a positive integer. In the above equation we use the following notation: $|G_1|$ is the number of group elements in subgroup G_1. $\vec{t}'$ represents a primitive translation in G_1. g' is a coset representative of the translations in G_1 and in general may contain a nonprimitive translation. $\chi^{(*\vec{k},m)}(g'\vec{t}')$ is the character of the group element $g'\vec{t}'$ in irrep. $D^{(*\vec{k},m)}$. The general form of the characters for the $\vec{\Gamma}$ and $\vec{F}$ points is

$$\chi^{(\vec{0},m)}=\chi$$

and

$$\chi^{(*\vec{F},m)}=(-1)^{\eta_1+\eta_2}\chi_1+(-1)^{\eta_2+\eta_3}\chi_2+(-1)^{\eta_1+\eta_3}\chi_3\ ,$$

respectively. Each term, e.g., $(-1)^{\eta_1+\eta_2}\chi_1$, is the contribution to the character from one arm of the $*\vec{F}$ with χ_1 arising from the coset representation in $R\bar{3}c$ and $(-1)^{\eta_1+\eta_2}$ arising from the translation of the form

$$\vec{t}'=\eta_1\vec{t}_1+\eta_2\vec{t}_2+\eta_3\vec{t}_3\ .$$

The forms of these characters when used in Eq. (1) yield translational subgroups among those given in Table I. Both primitive and nonprimitive lattices are shown. In addition the character forms when used in Eq. (1) demand a compatibility of coset representatives in G_1 with coset representatives and primitive translations in G^0. A translation and/or rotation of origin is often necessary in the correspondence. Finally the chain criterion (D') was applied.

TABLE II. Phase transitions in $R\bar{3}c$ structure which are consistent with Landau conditions.

Irrep.	Subduction frequency	Allowed subgroup (translational subgroup[a])
$D^{(*\vec{0},2)}$	1	$R\bar{3}(C_{3i}^2)$ (a)
$D^{(*\vec{0},3)}$	1	$R32(D_3^7)$ (a)
$D^{(*\vec{0},4)}$	1	$R3c(C_{3v}^6)$ (a)
$D^{(*\vec{0},6)}$	1	$Cc(C_s^4)$ (b); $C_2(C_2^3)$ (b);
	2	$P(1)(C_1^1)$ (a)
$D^{(*\vec{F},1)}$	1	$P2_1/c(C_{2h}^5)$ (a); $R\bar{3}(C_{3i}^2)$ (b); $C2(C_2^3)$ (c)
	2	$P\bar{1}(C_i^1)$ (b)
	3	$P1(C_1^1)$ (b)
$D^{(*\vec{F},2)}$	1	$P2_1/c(C_{2h}^5)$ (a); $R3c(C_{3v}^6)$ (b); $C_2(C_2^3)$ (c)
	2	$Cc(C_s^4)$ (c); $P\bar{1}(C_i^2)$ (b)
	3	$P1(C_1^1)$ (b)
$D^{(*\vec{F},4)}$	1	$P2/c(C_{2h}^4)$ (a); $R32(D_3^7)$(b)
	2	$C2(C_2^3)$ (c); $P\bar{1}(C_i^1)$ (b).
	3	$P1(C_1^1)$ (b)

[a]See Table I.

Table II shows the allowed symmetry groups arising from the $\vec{\Gamma}$ and $\vec{F}$ order parameters as obtained by the above process. Only these two $\vec{k}$ vectors can satisfy the complete set of symmetry conditions consistent with the Landau conditions. All of the allowed symmetry groups including nonprimitive as well as primitive structures arising from an $R\bar{3}c$ structure are included. The subgroups together with the forms of their translational subgroups are included for completeness.

IV. CONCLUSIONS

A systematic classification of phase transitions from the prototype $R\bar{3}c$ phase corresponding to a variety of points of the Brillouin zone has been developed. The Landau group-theoretical description of continuous transitions as formulated by Birman and Jarić allows only irreducible representations arising from the $\vec{\Gamma}$ and $\vec{F}$ points and the corresponding subgroups have been listed in Table II.

Transitions driven by the $\vec{\Gamma}$ point reduce to compatibility conditions of the *point* group $D_{3d}(\bar{3}m)$. The resulting allowed subgroups will be the same for any structure of the class D_{3d} if the transition can be associated with the $\vec{k}=0$ point. There are several such structures which can then be classified from Table II. For example sodium azide exists in a high-temperature β phase with $R\bar{3}m\,(D_{3d}^5)$ symmetry. It undergoes a phase transition near 293 K to a monoclinic α phase with symmetry $C2/m\,(C_{2h}^3)$. Both phases are symmorphic and can therefore be classified by point-group considerations. From our results $C2/m$ is not an allowed subgroup so the transition cannot be continuous. Experiment indicates that as a first-order transition it is only weakly so.[11] A similar description of the phase transition in *sym*-triazine indicates the $R\bar{3}c$ to $C2/c$ must be first order (although weakly so).[12]

Only one transition from the $R\bar{3}c$ structure which is driven by the $\vec{F}$ point is known to the author. The transition is calcite from $R\bar{3}c\,(D_{3d}^6)$ to $P2_1/c\,(C_{2h}^5)$ is allowed to be continuous by our classification. Some evidence of critical (continuous) phenomena has been indicated[23] although the continuous nature of that transition is not definite.

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