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Distortions in the D_{6h} Crystal Class to $a \times a\sqrt{3} \times c$ Orthorhombic Lattices

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The Landau theory of symmetry and phase transitions is used to determine the orthorhombic space groups with $a \times a\sqrt{3} \times c$ superlattice that can result from hexagonal symmetries in the crystal class D_{6h} via second-order symmetry-breaking transitions.

Introduction

Solid state chemists and materials scientists have shown increased interest in symmetry breaking phase transitions because of widespread interest in electron–phonon interactions, the interest of solid state theorists in soft-mode phenomena, and the availability of highly resolved X-ray diffraction data. One example of a well-studied symmetry breaking transition is the NiAs-type to MnP-type transition (*1–3*). An early interest in group–subgroup relations (*4*) has led to a wide interest in this aspect of Landau theory (*5–7*), but frequently the other aspects of the theory (the conditions that the transition correspond to a single irreducible representation, that there be no third-order invariants and no vector invariants (the Lifshitz condition)) are overlooked. The latter three are far more restrictive than the former, and have power in determining which symmetry breaking transitions can occur continuously. The Landau theory for the NiAs-type to MnP-type case shows that the transition from $P6_3/mmc$ to *Pnma* is allowed as a second-order transition. The question that arises from the point of view that centers on the group–subgroup condition is why does this distortion not occur continuously through the *Cmcm* space group, a subgroup of $P6_3/mmc$ and a supergroup of *Pnma*? This question is answered here for $P6_3/mmc$, and also for the other space groups in the class D_{6h}, from the point of view of Landau theory.

Landau Theory

The transition from a space group in the D_{6h} crystal class to one of the orthorhombic crystal classes (D_2, C_{2v}, or D_{2h}) in which the orthorhombic lattice is simply a distortion of the hexagonal lattice without loss of translational symmetry operations (i.e., a distortion at $\vec{K} = 0$ resulting in an end-centered orthorhombic cell, such as

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TABLE I

E	C_{6z}	C_{2y}	i
$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} \omega & 0 \\ 0 & \omega^5 \end{bmatrix}$	$\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$
$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} \omega & 0 \\ 0 & \omega^5 \end{bmatrix}$	$\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$	$\begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}$
$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -\omega & 0 \\ 0 & -\omega^5 \end{bmatrix}$	$\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$
$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -\omega & 0 \\ 0 & -\omega^5 \end{bmatrix}$	$\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$	$\begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}$

$P6_3/mmc$ $\rightarrow$ *Cmcm*) can be analyzed by Landau theory by examining the irreducible representations of the space groups of the D_{6h} class at $\vec{K} = 0$. These irreducible representations are the same for all groups in the class, and are the same as those of the point group D_{6h}.

The one-dimensional representations that correspond to distortions (all except the totally symmetric) yield crystal classes with half the number of essential symmetry operations of D_{6h}, i.e., 12 essential operations. Since the orthorhombic classes have 4 or 8 essential operations, the one-dimensional irreducible representations cannot result in orthorhombic distortions.

The four two-dimensional irreducible representations (Table I) yield two monoclinic distortions (the first two rows) and two orthorhombic distortions (the last two rows). The fourth row yields *Cmcm* in the case of *$P6_3/mmc$*. However the question of whether or not these irreducible representations can result in continuous transitions is answered by the third and fourth conditions of Landau.

In the case of a transition from D_{6h} to D_{2h} with no loss in translational symmetry (the case of row 4 of Table I) there is a change by a factor of 3 in the number of symmetry operations, a change that requires the existence of a third-order invariant (*7, 8*). Thus, a transition from a hexagonal centrosymmetric structure to an orthorhombic centrosymmetric structure cannot occur continuously without loss of translational periodicity. If a loss of centrosymmetricity occurs then the change is by a factor of 6 and the fact that the basis functions change sign under inversion (row 3 of Table I) implies that a third-order invariant does not exist. Thus, the transitions from D_{6h} to D_2 implied by this row meet Landau's third condition.

The fourth, or Lifshitz, condition is met at $\vec{K} = 0$ if $\Sigma(\chi^2(y) - \psi(g^2))v(R) = 0$, where the sum is over all symmetry operations of D_{6h}, σ is the character of the operation g (or g^2), and $V(R)$ is the character of the vector representation (*7*). A calculation of this sum using the appropriate values from row 3 of Table I shows that a "zellengleich" transition from D_{6h} to D_2 is allowed. The cases in which the principle axis is a 6_3 axis yield $C222_1$ symmetry and the 6 axis cases yield *C*222 symmetry.

The remaining allowed continuous distortions to yield the orthorhombic lattice in question must be accompanied by superstructure formation, i.e., must yield primitive cells. The irreducible representations in question correspond to the $\vec{K} = \vec{a}/2$ special point of the Brillouin zone. All of the irreducible representations in question are one dimensional and straight forwardly meet the third and fourth conditions. The allowed orthorhombic space groups, which are listed in Table II, are all centrosymmetric.

TABLE II

P6/mmm	*Pmmm, Pban, Pbam, Pmmn, Pmna, Pmma*
P6/mcc	*Pccm, Pnnn, Pmna, Pnnm, Pccn*
$P6_3/mcm$	*Pmma, Pnna, Pbcn, Pmmn, Pnnm, Pbcm, Pnma*
$P6_3/mmc$	*Pmma, Pnna, Pbcn, Pmmn, Pnnm, Pbcm, Pnma*

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