The Symmetry of Quasiperiodic Crystals

A Dissertation
Presented to the Faculty of the Graduate School
of Cornell University
in Partial Fulfillment of the Requirements for the Degree of
Doctor of Philosophy

by
Ron Yitzhak Lifshitz
August 1995

The Symmetry of Quasiperiodic Crystals

Ron Yitzhak Lifshitz, Ph.D.

Cornell University 1995

It is shown that the Fourier-space reformulation of the conventional symmetry classification of crystals, which abandons the traditional reliance on periodicity, not only unifies the treatment of periodic and quasiperiodic crystals but also provides for a unified treatment of the various types of quasiperiodic crystals — modulated crystals, composite crystals, and quasicrystals. The approach is more coherent than the conventional high-dimensional "superspace" approach (which treats the types of quasiperiodic crystals differently, producing a separate classification for each type) and has the added benefit of working in three dimensions. As a pedagogical example, a complete enumeration of all Bravais classes for the simplest incommensurate reducible lattices — all 3-dimensional rank-4 Bravais classes and all 3-dimensional rank-6 cubic and tetrahedral Bravais classes — is given. This is followed by a classification of all Bravais classes and space groups for hexagonal and trigonal crystals of arbitrary finite rank. In the process, general techniques for the enumeration of Bravais classes and space groups are illustrated.

BIOGRAPHICAL SKETCH

Ron Lifshitz was born in Jerusalem in 1964. In 1982 he graduated from high school and joined the Israel Defense Forces where he served for a period of five years. In the fall of 1987 he moved back to Jerusalem with Nurit, whom he married in the spring of 1988. During the next three years Ron studied at the Hebrew University of Jerusalem where he earned his B.Sc. degree in Physics and Computer Science. Ron and Nurit moved to Ithaca in the fall of 1990. Since then Ron has been a graduate student in the Laboratory of Atomic and Solid State Physics at Cornell University, where he has worked with David Mermin on various projects related to the subject of this dissertation. During their stay in Ithaca, Ron and Nurit had two children — Adee, who was born on a snowy day in the winter of 1993, and Noam, who was born on a snowy day in the spring of 1994. Ron plans to move with his family to Pasadena where he will take a position as a postdoctoral research fellow at the California Institute of Technology.

To Nurit

ACKNOWLEDGEMENTS

I am grateful to many people for their help, support, and friendship during my five year stay at Cornell.

I would like to begin by thanking David Mermin who during all these years has been a patient teacher and an inspiring collaborator. I greatly benefited from his unbiased and clear thinking and from his originality. From him I learned that only when you start writing up the results of your research do you realize that you have not even begun to understand them. From him I learned that writing clearly is no less important than carrying out the research itself. From him I learned that things are usually not as simple as one would expect them to be. From him I learned that it is better first to try to understand things by myself and only later become influenced by previously "established results". His faith in me was, and still is, a great source of confidence. For all this and for his true friendship, I thank him.

I thank Jim Sethna for his special interest in me and in my work and for his willingness to become a member of my special committee at a time when he had more students than the hand could count. His comments and suggestions at various stages of my work were extremely valuable. I am grateful for his friendship and for his personal advice on numerous issues, especially for suggesting David Mermin as a thesis advisor. His enthusiasm is to be admired.

Dave Lee has been the only five-year member of my special committee, seeing me through all stages of my graduate career. I thank him for his wonderful spirit and good humor as well as his encouraging words on many occasions.

I thank Veit Elser and Chris Henley for leading the "Quasicrystal Group" and for showing interest in my work. I am grateful for a number of enlightening discussions with them regarding the work presented in this dissertation and also my work on magnetic symmetry and on color symmetry. I thank Chris Henley also for a great Solid State II course — the only solid state course I ever took.

During the last year I had the opportunity to travel to a number of conferences where I had useful discussions with many people on subjects related to my research. I would like specifically to thank Sander van Smaalen, J. Manuel Perez-Mato, Michael Baake, Marko Jarić, and Marjorie Senechal.

I thank the Physics Department staff, especially Debbie Hatfield and Cindy LeFever, whose help on numerous occasions saved me a great deal of trouble. I would also like to thank my fellow graduate students in the Physics Department and in LASSP for their part in creating such a wonderful working environment.

I thank my office mates in 616 Clark, Jané Kondev, Rob Phillips, Jan von Delft, Chen Zeng, and Claudia Filippi for bearing with me all these years and for reading drafts of my papers, and listening and commenting on my lengthy, and often boring arguments in group theory. I am especially grateful to Jané and Rob for their friendship and support during tough times.

I thank the Cornell Materials Science Center and the Sproul Fund for their financial support of my conference travels. I thank the National Science Foundation for its support of my research through grants DMR 89-20979 and DMR 92-22792.

TABLE OF CONTENTS

LIST OF TABLES

Chapter 1

Introduction

1.1 Quasiperiodic Crystals

1.1.1 Definitions

Nine years after the discovery of the first quasicrystal[1] the International Union of Crystallography established a Commission on Aperiodic Crystals in whose terms of reference[32, page 928] a new definition was given to crystal:

> "...by *crystal* we mean any solid having an essentially discrete diffraction diagram, and by *aperiodic crystal* we mean any crystal in which three-dimensional lattice periodicity can be considered to be absent."

The definition was intentionally made vague by the inclusion of the word "essentially". It was meant only as a temporary working-definition until a better understanding of crystallinity emerges. We shall adopt it for the purpose of our analysis here. We shall only consider crystals whose diffraction patterns — the Fourier spectrum of their density functions — can be expressed as a sum of delta functions and rely on the word "essentially" to rescue us from the problems of diffraction patterns that in the limit of infinite experimental resolution would densely fill all of 3-dimensional Fourier space. We shall refer to such aperiodic crystals as *quasiperiodic crystals*.[2] We shall normally be interested in quasiperiodic crystals whose diffraction diagrams can be indexed by a finite number of integers. This number is the rank of the crystal (to be properly defined later).

Although an official nomenclature has not yet been established, one clearly distinguishes between different kinds of quasiperiodic crystals: incommensurately mod-

[1] The first AlMn icosahedral quasicrystal was discovered by Dan Shechtman on April 8, 1982. The first official announcement on the pages of *PRL* came only two years later[25].

[2] In its broadest definition, an aperiodic crystal might contain other terms in its Fourier spectrum in addition to the sum of delta functions. As defined here, the density of quasiperiodic crystals is an *almost periodic function* of $\mathbf{r}$, as defined by Bohr[2].

ulated crystals, incommensurate composite crystals, and quasicrystals. We should clarify what *we* shall mean by these terms.[3]

The simplest quasiperiodic crystal is an *incommensurately modulated periodic crystal*. It can be considered as a periodic basic (or average) structure which is perturbed in a periodic way ("modulated"), with the period of the perturbation being incommensurate with the underlying periodicity of the basic structure. The nature of the perturbation is usually a periodic displacement of the atomic positions or a periodic variation in the occupation probability of the atomic sites. The diffraction diagrams of incommensurately modulated periodic crystals are characterized by having a subset of "main reflections" — Bragg peaks which are brighter than the others — that can be indexed by three integers and forms an ordinary commensurate reciprocal lattice. This lattice describes the periodicity of the average periodic structure. The weaker peaks, called "satellites", describe the periodicity of the modulation.

Incommensurate composite crystals, also called intergrowth compounds[4] can be considered as composed of two or more interpenetrating subsystems with mutually incommensurate periodicities. Each subsystem when viewed independently is itself a crystal — in all known examples a periodic one — which is incommensurately modulated due to its interaction with the other subsystems. Examples of composite crystals are *misfit layer structures* which consist of alternating layers of the different subsystems where the periodicity within the layers of one subsystem is incommensurate with those of the other subsystems. There are also *channel-type structures* which possess one host structure containing channels in which the other subsystem(s) are accommodated. The diffraction diagrams of composite crystals are characterized by the existence of two or more subsets of main reflections, forming commensurate reciprocal lattices, caused by the average structures of the periodic subsystems, and a set of weak reflections caused by their modulations. Because the modulation of each subsystem is caused by the average structures of the others, weak reflections appear at wave vectors that are integral linear combinations of main reflections associated with different subsystems.

There are also quasiperiodic crystals for which a description in terms of a modulation of a basic structure or a composition of two or more substructures is either inappropriate or impossible. In these crystals the underlying order is itself quasiperiodic. The best model for such crystals is a quasiperiodic tiling such as the famous Penrose tiling. One fills space with "unit cells" or "tiles" in a way that maintains long range order (and produces a discrete diffraction diagram) without being periodic. The observed icosahedral quasicrystals as well as the octagonal,

[3]For a recent review on quasiperiodic crystals see van Smaalen[26]. Our definitions of the different kinds of quasiperiodic crystals differ from the ones given there in two ways: (1) Van Smaalen requires the average structure of a modulated crystal and the subsystems of a composite crystal to be periodic; (2) He defines quasicrytals as crystals with non-crystallographic point groups.

[4]We follow here the nomenclature used by van Smaalen[28].

decagonal, and dodecagonal quasicrystals fall under this category. We also know of examples of quasiperiodic crystals with cubic symmetry(see Feng *et al.*[6]), and possibly also examples with tetrahedral (see Donnadieu[4] and Dräger *et al.*[5]) and with hexagonal (see Selke *et al.*[23]) symmetry, that are neither modulated crystals nor composite crystals. We refer to all such quasiperiodic crystals as *quasicrystals* but warn the reader that this is not the standard use of the term. In most of the literature "quasicrystal" refers *only* to quasiperiodic crystals which violate the so-called "crystallographic restriction", *i.e.* those which have an n-fold axis of symmetry with $n = 5$ or $n \geq 7$.

Finally, one can of course have incommensurately modulated quasicrystals (see Denoyer *et al.*[3] and Menguy *et al.*[13]), where a quasiperiodic basic structure is incommensurately perturbed. One can also, at least theoretically, construct composite crystals where the subsystems are themselves already quasiperiodic.

1.1.2 The Symmetry Classification of Quasiperiodic Crystals

The conventional extension of the space-group classification scheme to quasiperiodic crystals, was developed and used by de Wolff, Janssen, and Janner[29,31,8, henceforth JJdW] to classify "The superspace groups for incommensurate crystal structures with a one-dimensional modulation", long before the discovery of the first icosahedral quasicrystal. Their approach retains the old criterion of periodicity as the starting point for a crystallographic classification scheme by treating quasiperiodic structures as 3-dimensional sections of structures periodic in a higher-dimensional "superspace". The superspace approach describes the symmetry of incommensurately modulated crystals using a subclass of high-dimensional space groups which satisfy certain reducibility requirements so that no symmetry operation mixes main reflections and satellites. The superspace approach, which was originally developed for treating incommensurately modulated crystals, has since been extended to deal also with composite crystals (see Janner and Janssen[7], Yamamoto[30], and van Smaalen[27,28]) and with quasicrystals (see Janssen[9]. We shall have more to say later about these extensions.

The discovery of icosahedral quasicrystals has motivated an alternative generalization of the space-group classification scheme that does not rely on spatial periodicity. It is applicable to both periodic and quasiperiodic structures in 3-dimensional space, without having to treat them as 3-dimensional slices of higher dimensional periodic structures, as is done in the superspace approach. This is accomplished by reformulating conventional crystallography in Fourier space, where it becomes a symmetry based classification scheme for diffraction patterns consisting of sharp Bragg peaks in line with the new definition of crystal. When those diffraction patterns can be indexed by three integers, the general scheme reduces to the ordinary crystallographic space-group classification; but the same three-dimensional scheme works just as well for the diffraction patterns of quasiperiodic materials,

which require more than 3 integers for their indexing. The shift to Fourier space of the crystallographic classification scheme was proposed over thirty years ago by Bienenstock and Ewald[1] and established as a practical scheme for periodic and quasiperiodic crystals by Rokhsar, Wright, and Mermin[21,22], with later contributions by Rabson, Ho, Dräger, and Lifshitz.[5]

The Fourier-space approach has been applied to a simple and unified enumeration of the space groups for all periodic crystals and all standard[6] quasicrystals whose rank[7] is the smallest compatible with their point group (See Rabson *et al.*[19] and Mermin[14]).

The purpose of this thesis is to demonstrate the application of the Fourier-space approach to the symmetry classification of the remaining types of quasiperiodic crystals. We shall establish that the Fourier-space approach is applicable to the classification of incommensurately modulated crystals and composite crystals, providing a unified scheme for all the types of quasiperiodic crystals.

In the remaining of this chapter we shall give an introduction to Fourier-space crystallography. In the chapters that follow we shall present the approach more completely and apply it to the symmetry classification of crystals whose diffraction diagrams are indexed by more integers than the minimum required by their point group. Such diffraction patterns may contain one or more subsets of bright Bragg peaks which form commensurate reciprocal lattices.

1.2 Fourier-Space Crystallography

1.2.1 The Bravais Class — A Class of (Reciprocal) Lattices

Each Bragg peak in the discrete diffraction pattern determines a wave vector $\mathbf{k}$ at which the density has a nonvanishing coefficient in its Fourier expansion,

$$\rho(\mathbf{r}) = \sum_{\mathbf{k}\in L} \rho(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}} \ . \tag{1.1}$$

The (reciprocal) *lattice* L — called by some the Fourier module or the $\mathbb{Z}$-module — is defined as the set of all integral linear combinations of the wave vectors determined by the observed Bragg peaks. As so defined, L includes wave vectors at which the coefficients $\rho(\mathbf{k})$ are too weak to be detected. As the resolution is improved more peaks may appear at larger wave vectors and in the quasiperiodic case between already existing peaks. This is because quasiperiodic lattices are 'dense' in the mathematical sense — there is no requirement of minimal distance between wave vectors. The lattice L may also include wave vectors at which $\rho(\mathbf{k})$ is required to

[5] For a recent review see Mermin[14].

[6] A quasicrystal can be non-standard only if it contains a symmetry axis that is at least 23-fold.

[7] The rank, to be defined shortly, is the minimum number of integers needed to index the diffraction pattern.

vanish by the symmetry of the crystal. Such points are called extinctions and will be discussed later.

We normally restrict ourselves to lattices which are integral linear combinations of a *finite* number of wave vectors. The minimum number D of vectors needed to generate L is called the *rank* or indexing dimension of L. A crystal is *periodic* if and only if the rank of its lattice is equal to the physical dimension d. Only then is the lattice a conventional 'reciprocal lattice' related in the familiar way to a lattice of real-space translations under which the periodic crystal is invariant. We shall always use the term 'lattice' to refer to the rank-D lattice of wave vectors and not to any direct lattice of translations in ordinary (or higher-dimensional) real space.

The point group of the lattice — its holohedry — is the set of proper and improper rotations applied about the origin of Fourier space which leave the lattice invariant. We shall consider only finite subgroups of $O(3)$ and require that they contain the inversion because the negative of every lattice vector is in the lattice.

Lattices are classified into Bravais classes. Two lattices are in the same *Bravais class* if one can interpolate between them with a sequence of lattices, all with the same point group and rank. We shall discuss this equivalence criterion for lattices more deeply in section 2.2.2. We only mention at this point that the relative intensities of the Bragg peaks associated with the lattice wave vectors does not come into this definition of Bravais class.

The relative intensities of the Bragg peaks *can* be used to distinguish between the various types of quasiperiodic crystals introduced in section 1.1. Quasiperiodic crystals fall under three categories based on their Bragg peak intensities: The term *quasicrystal* is used for quasiperiodic crystals in which no clear distinctions can be made between the Bragg peaks based on their intensity (other than the general tendency of peaks with higher indices to have lower intensities); The diffraction patterns of *incommensurately modulated crystals* contain a single sublattice of strong reflections ("main reflections") caused by an average periodic or quasiperiodic structure and a set of weak reflections ("satellites") caused by the modulations; *Composite crystals*, which are composed of two (or more) interpenetrating subsystems, produce two (or more) sublattices of main reflections and a set of satellites which are due to the mutual interaction of the subsystems.

1.2.2 Indistinguishability and the Concept of Point Group Symmetry

The point group of a periodic crystal is traditionally defined as the subgroup of the lattice point group that leaves the density itself invariant to within a translation. The densities of quasiperiodic crystals, however, in general possess no such symmetries. In fact, it is not hard to show that if a two-dimensional crystal does contain more than a single point, about which an n-fold rotation ($n > 2$) brings it into perfect coincidence with itself, then the crystal is necessarily periodic. What one

observes in the quasiperiodic case is that any region in a rotated quasiperiodic crystal can be found in the unrotated crystal, but the larger the region the further away you have to look in order to find it. The two crystals contain the same statistical distribution of substructures on all scales.

Two densities that are statistically the same in this sense though not necessarily identical are called *indistinguishable*, and the *point group* of a crystal is redefined as the set of rotations that take the density into an indistinguishable one. The precise mathematical condition for densities ρ and ρ' to be indistinguishable is that they have the same positionally averaged n-point autocorrelation functions for all n –

$$\frac{1}{V}\int d\mathbf{r}\rho(\mathbf{r}_1-\mathbf{r})\ldots\rho(\mathbf{r}_n-\mathbf{r}) = \frac{1}{V}\int d\mathbf{r}\rho'(\mathbf{r}_1-\mathbf{r})\ldots\rho'(\mathbf{r}_n-\mathbf{r}) \ . \tag{1.2}$$

We shall show in section 3.2 that this condition acquires a very simple form in Fourier space — the Fourier coefficients of two indistinguishable densities ρ and ρ' must be related by

$$\rho'(\mathbf{k}) = e^{2\pi i\chi(\mathbf{k})}\rho(\mathbf{k}) \ , \tag{1.3}$$

where $\chi(\mathbf{k})$, called a *gauge function*, is linear modulo an integer over the lattice of wave vectors (*i.e.* $\chi(\mathbf{k}_1+\mathbf{k}_2) \equiv \chi(\mathbf{k}_1)+\chi(\mathbf{k}_2)$ whenever $\mathbf{k}_1$ and $\mathbf{k}_2$ are in the lattice, where "$\equiv$" indicates equality modulo an integer).

In the periodic case one can show that $2\pi\chi(\mathbf{k})$ is necessarily of the form $\mathbf{k}\cdot\mathbf{d}$ for some constant vector $\mathbf{d}$ independent of $\mathbf{k}$, so that $\rho'(\mathbf{r}) = \rho(\mathbf{r}+\mathbf{d})$ and indistinguishability reduces back to identity to within a translation. One can then combine point group operations with translations to recover the traditional space groups of periodic crystals, containing operations that leave the density *identical* to what it was. In the quasiperiodic case one must retain the general form of $\chi(\mathbf{k})$ which is defined only on the lattice and cannot be linearly extended to arbitrary $\mathbf{k}$.

Because the point group is defined to leave the density indistinguishable, we can associate with each point group operation g a gauge function $\Phi_g(\mathbf{k})$, called a *phase function*, which relates $\rho(g\mathbf{k})$ and $\rho(\mathbf{k})$:

$$\rho(g\mathbf{k}) = e^{2\pi i\Phi_g(\mathbf{k})}\rho(\mathbf{k}) \ . \tag{1.4}$$

Since $\rho([gh]\mathbf{k}) = \rho(g[h\mathbf{k}])$, it follows directly from (1.4) that the set of phase functions associated with the elements of a point group G must satisfy the *group compatibility condition:*

$$\forall g,h\in G: \qquad \Phi_{gh}(\mathbf{k}) \equiv \Phi_g(h\mathbf{k}) + \Phi_h(\mathbf{k}). \tag{1.5}$$

These constraints on the phase functions are the generalizations to quasiperiodic crystals of the Frobenius congruences in the traditional space group description of periodic crystals (See for example Senechal[24, page 69]. One can use (1.5), for example, to show that if g and h commute their phase functions must satisfy $\Phi_g([h-1]\mathbf{k}) \equiv \Phi_h([g-1]\mathbf{k})$.

The term *crystallographic point groups* is used to refer to the 32 point groups that may also describe the symmetry of periodic crystals, *i.e.* those which do not contain an axis of n-fold symmetry with $n = 5$ or $n \geq 7$. This term is used for historical reasons.[8]

1.2.3 The Space Group — A Class of Phase Functions

The symmetry classification of crystals is an organization of sets of phase functions into equivalence classes according to two criteria:

1. Gauge Equivalence. Two sets of phase functions, Φ and Φ', that describe indistinguishable densities ρ and ρ', related by a gauge function χ, are associated with the same symmetry class. It follows from (1.3) and (1.4) that two such sets must be related by

$$\Phi'_g(\mathbf{k}) \equiv \Phi_g(\mathbf{k}) + \chi([g-1]\mathbf{k}) \tag{1.6}$$

for every g in the point group and every $\mathbf{k}$ in the lattice.[9] We call phase functions describing indistinguishable densities *gauge-equivalent* and equation (1.6), converting Φ into Φ', a *gauge transformation*.

2. Scale Equivalence. Two sets of phase functions, Φ and Φ', are also counted as equivalent if there is a symmetry s of the lattice L, which is an automorphism of the point group $G = sGs^{-1}$, taking one set into the other

$$\Phi'_g(\mathbf{k}) = \Phi_{sgs^{-1}}(s\mathbf{k}) \ . \tag{1.7}$$

Operations s that are in the point group G of the crystal have precisely this property, but one can show directly from (1.5) that for such s, Φ' and Φ are already gauge-equivalent. If s is *not* an element of the point group G, then the two sets of phase functions will not in general be gauge-equivalent. In the periodic case s can be an element of $O(3)$ (for example a 90 degree rotation when G is a tetrahedral point group on a cubic lattice), or an element of $O(3)$ combined with a rescaling of the primitive lattice-generating vectors (for example 90 degree rotations of an orthorhombic lattice). Here the distinct gauge-equivalence classes making up a single space group are the different settings of that space group. In the quasiperiodic case s can be an isotropic rescaling of the entire lattice (as in icosahedral quasicrystals), an isotropic rescaling of a sublattice (as in axial quasicrystals), or even independent rescalings of individual lattice-generating vectors. Because rescalings are often (though not always) a part of the transformation s, two classes of gauge-equivalent phase functions that are further identified in this manner are called *scale-equivalent*.

The classes of phase functions under gauge equivalence and scale equivalence correspond precisely to the space groups in the periodic case, and constitute the

[8] Note the unfortunate but true statement that the point group of a crystal is not necessarily a crystallographic point group.

[9] By $[g-1]\mathbf{k}$ we simply mean the difference of the two vectors $g\mathbf{k} - \mathbf{k}$.

extension of the space group classification scheme to the general quasiperiodic case. We continue to call them space groups even though they are only equivalence classes of phase functions and no longer subgroups of the Euclidean group $E(3)$. Nevertheless, they may be given an algebraic structure of a group consisting of ordered pairs (g, Φ_g) as shown by Rabson, Ho, and Mermin[18].

1.2.4 Gauge Invariant Phases — Screw Axes, Glide Planes, and Extinctions

It follows from Eq. (1.6) that if $g\mathbf{k} = \mathbf{k}$ then $\Phi_g(\mathbf{k})$ is invariant under arbitrary gauge transformations. These gauge-invariant phases are directly related to the phenomenon of *extinctions*, for it follows directly from the definition (1.4) of the phase function that whenever $g\mathbf{k} = \mathbf{k}$, the Fourier coefficient $\rho(\mathbf{k})$ vanishes unless $\Phi_g(\mathbf{k})$ also vanishes (modulo an integer). Thus the phase functions of a given space group immediately determine the extinctions. It has been shown by Mermin[15] that there is no other generic reason for wave vectors in the lattice to be missing from the Fourier expansion of the density.

Extinctions have a somewhat different character when viewed from the perspective of Fourier space. Traditional crystallography starts with a direct lattice of translations, dual to this lattice is a lattice of wave vectors, and associated with each wave vector is a Bragg peak. Certain Bragg peaks may be missing from the diffraction pattern as a consequence of special symmetry elements of the space group – screw axes and glide planes. In Fourier-space crystallography one begins with the observed diffraction pattern and extends it by taking all integral linear combinations of observed wave vectors to form the lattice. Every lattice vector is a candidate for an additional Bragg peak unless the associated Fourier coefficient is required by the space group to vanish. The emphasis thus shifts from extinctions as missing Bragg peaks to extinctions as peaks that can never be added to the diffraction pattern no matter how much the resolution is improved.

One can easily show by using the group compatibility condition (1.5) that a phase function associated with a mirror m can only assume the values 0 and 1/2 in the invariant plane of the mirror, and that a phase function associated with an n-fold rotation r can only assume the values j/n on the axis of rotation.

We call the plane of a mirror m a *glide plane* if $\Phi_m(\mathbf{k}) \not\equiv 0$ for any lattice vector in the plane. We call the axis of a rotation r a *screw axis* if $\Phi_r(\mathbf{k}) \not\equiv 0$ for any lattice vector on the axis. These definitions eliminate the need to associate extinctions with the interplay between rotations and translations which is peculiar to the periodic case.

1.3 Enumeration — What to Expect in the Following Chapters

1.3.1 Bravais Classes

Enumerating all Bravais classes of lattices of a given point group and rank can be a highly non-trivial task. Consider for example the case of 2-dimensional N-fold symmetric lattices whose rank is the smallest compatible with their point group (N is necessarily even because in two dimensions the inversion is equivalent to the 2-fold rotation and all lattices have inversion symmetry). The simplest lattices are given by all integral linear combinations of N unit vectors separated in angle by $2\pi/N$ and are called *standard lattices*. Mermin, Rokhsar, and Wright[17] showed that a mapping of the enumeration problem to the mathematical theory of cyclotomic integers (all integral linear combinations of the N-th roots of unity) reveals a surprising result. All 2-dimensional N-fold symmetric lattices (of lowest rank) are equivalent to the standard lattices for all N from 4 to 44 and for N = 48, 50, 54, 60, 66, 70, 84, and 90. For all other N there are also non-standard lattices and the number of Bravais classes into which they are classified can be enormous (for example 359,057 for $N = 128$). Though real crystals are not known to exist with axes of symmetry of such high order, one should not take lightly the statement, for example, that all 12-fold lattices of rank 4 belong to one Bravais class.

With this word of caution in mind we can go ahead and try to develop some systematic techniques for the enumeration of Bravais classes. In Chapter 2 we introduce such a technique which is called the "modular lattice method". Simply stated it requires one to find a common sublattice for all lattices of a given rank and point group, and then to consider all the distinct ways of adding lattice points to construct the full lattice. This way of looking at all possible lattices corresponds, for example, to viewing each rank-3 cubic lattice as a simple cubic lattice with a basis.

We shall use the modular lattice method in Chapter 2 to enumerate all the 3-dimensional rank-4 Bravais classes and all the 3-dimensional rank-6 cubic and tetrahedral Bravais classes.[10] These are the simplest *reducible* incommensurate lattices, all with crystallographic point groups. By "reducible" we mean that they can be expressed as integral linear combinations of vectors from a rank-3 sublattice, independently invariant under the point group, and vectors from an additional rank-1 (or in the cubic and tetrahedral case, rank-3) lattice. Such lattices are the simplest lattices that can describe the symmetry of incommensurately modulated crystals or composite crystals, whose symmetry classification is the main objective of this thesis.

It will be shown that all these Bravais classes except for three rank-6 tetrahedral

[10] The enumeration of these Bravais classes appears also in Mermin and Lifshitz[16].

Bravais classes contain lattices which are not only reducible but also *decomposable*, meaning that the additional rank-1 (or in the cubic and tetrahedral case, rank-3) lattice is also independently invariant under the point group. For example, the rank-6 cubic lattices are all sums of two of the well-known rank-3 cubic lattices. As such they are classified into six Bravais classes denoted by the two constituent rank-3 Bravais classes as: $P+P$, I^*+I^*, F^*+F^*, $P+F^*$, $P+I^*$, and I^*+F^* (the star is a reminder that the body centered (I^*) or face centered (F^*) lattices are so centered in Fourier space). The three Bravais classes of rank-6 tetrahedral lattices cannot be decomposed in such a way since we know that there are no tetrahedral lattices of rank 3, yet they are 3+3 reducible. Lattices in these three Bravais classes are most simply described as integral linear combinations of the six vectors $(1, \pm\alpha, 0)$, $(0, 1, \pm\alpha)$, and $(\pm\alpha, 0, 1)$ with primitive, face-centered (the sum of all integers even) and body-centered (all integers of the same parity) indexing. When the irrational number α is equal to the golden mean these become the three Bravais classes of rank-6 icosahedral crystals (see Rokhsar, Mermin and Wright[20]).

In Appendix A we shall establish that all hexagonal and trigonal lattices of arbitrary (but finite) rank are decomposable into only three types of periodic building blocks: rank-1 sublattices along the axis of 3- or 6-fold symmetry, rank-2 triangular sublattices in the plane perpendicular to the axis of rotation, and — only in the trigonal case — rank-3 rhombohedral sublattices. We use this property of the lattices in Chapter 4 to enumerate all hexagonal and trigonal Bravais classes of rank-n by simply considering all possible decompositions of n and all distinct mutual orientations of the various constituent sublattices.

In the examples above one sees the power of being able to use 3-dimensional geometry. Arriving at some of these results using the superspace approach would require knowledge of traditional crystallography in arbitrarily high dimensions.

1.3.2 Gauge-Equivalence Classes

When the lattice of wave vectors has finite rank the procedure for determining the possible phase functions is straightforward because they need be specified only by their values at the lattice-generating vectors (due to their linearity), and only for a set of elements g sufficient to generate the point group G (due to the group compatibility condition). These values are constrained by applying the group compatibility condition to the point group generating relations. By making a judicious choice of gauge one can simplify the calculation from the start by setting many of the unknown phases to zero, extracting a unique representative for each class of gauge-equivalent phase functions.

In Chapter 3 we shall determine, as a pedagogical example, the gauge equivalence classes for the rank-4 hexagonal and trigonal lattices, and in Chapter 4 for all hexagonal and trigonal lattices of arbitrary finite rank. We shall emphasize that when the lattice is decomposable into a sum of sublattices of lower-rank, each inde-

pendently invariant under the lattice point group, it is not necessary to recompute the possible gauge-equivalence classes for the high-rank lattice. One only needs to consider all the different combinations of the gauge-equivalence classes already classified for the lower-rank sublattices. This is possible because the group compatibility condition (1.5) acts independently in each invariant sublattice and the choice of gauge is independent in each invariant sublattice.

1.3.3 Scale-Equivalence Classes

The remaining part of the space group classification is merely a matter of simplifying the bookkeeping by grouping together different gauge-equivalence classes which are scale-equivalent. Although the grounds for this further identification are stated quite precisely, whether one chooses to make it or not can be a matter of convention. In non-centrosymmetric point groups, for example, the inversion is a symmetry of the lattice which can be used to relate gauge-inequivalent phase functions. In the periodic case, one normally chooses not to make this identification (because the inversion is not sense preserving), counting enantiomorphic pairs of gauge-equivalence classes as distinct space groups.

In Chapters 3 and 4 we shall also consider the scale-equivalence classes of phase functions for the hexagonal and trigonal lattices thus enumerating all the space groups.[11] When dealing with incommensurately modulated crystals or composite crystals one may wish to constrain the rescaling operations s to those which leave invariant the sublattice(s) of main reflections. The finer categories that arise by imposing such a constraint are considered as settings of the more general categories — the space groups. Different settings of a space group which are appropriate for the description of incommensurately modulated crystals or composite crystals are specified by identifying the sublattice(s) of main reflections.

[11] The results contained in these chapters appear in Lifshitz and Mermin[10,11].

Bibliography

[1] A. Bienenstock, and P. P. Ewald, "Symmetry of Fourier space", *Acta Cryst.* **15** (1962) 1253–1261.

[2] H. Bohr, "Almost periodic functions", (Chelsea, New-York, 1947).

[3] F. Denoyer, P. Launois, T. Motsch, and M. Lambert, "On the phase transition mechanism in Al–Cu–Fe: structural analysis of the modulated quasicrystalline and of the microcrystalline states", *J. Non-Cryst. Solids* **153 & 154** (1993) 595–599.

[4] P. Donnadieu, "The deviations of the Al_6Li_3Cu quasicrystal from icosahedral symmetry: a reminiscence of a cubic crystal", *J. Phys. I France* **4** (1994) 791–799.

[5] J. Dräger, R. Lifshitz and N. D. Mermin, "Tetrahedral Quasicrystals". To appear in the proceedings of the 5th International Conference on Quasicrystals, Avignon, France, May 22–26, 1995.

[6] Y. C. Feng, G. Lu, H. Q. Ye, K. H. Kuo, R. L. Withers, and G. Van Tendeloo, "Experimental evidence for and a projection model of a cubic quasicrystal", *J. Phys.: Condens. Matter* **2** (1990) 9749–9755.

[7] A. Janner and T. Janssen, "Symmetry of incommensurate crystal phases. II. Incommensurate basic structure", *Acta Cryst.* A**36** (1980) 408–415.

[8] T. Janssen, A. Janner, A. Looijenga-Vos, and P. M. de Wolff, "Incommensurate and commensurate modulated structures", *International Tables for Crystallography, Volume C,* Ed. A. J. C. Wilson, (Kluwer Academic, Dodrecht, 1992) 797–844.

[9] T. Janssen, "Crystallography of quasi-crystals", *Acta Cryst.* A**42** (1986) 261–271.

[10] R. Lifshitz and N. D. Mermin, "Space Groups of Trigonal and Hexagonal Quasiperiodic Crystals of Rank 4", *Acta Cryst.* A**50** (1994) 72–85.

[11] R. Lifshitz and N. D. Mermin, "Bravais Classes and Space Groups for Trigonal and Hexagonal Quasiperiodic Crystals of Arbitrary Finite Rank". *Acta Cryst.* A**50** (1994) 85–97.

[12] R. Lifshitz and N. D. Mermin, "The Symmetry of Composite Crystals". To appear in *Aperiodic '94, An International Conference on Aperiodic Crystals,* Ed. G. Chapuis (World Scientific, Singapore 1995).

[13] N. Menguy, M. de Boissieu, P. Guyot, M. Audier, E. Elkaim, and J. P. Lauriat, "Modulated icosahedral Al–Fe–Cu phase: a single crystal x-ray diffraction study", *J. Non-Cryst. Solids* **153 & 154** (1993) 620–622.

[14] N. D. Mermin, "The space groups of icosahedral quasicrystals and cubic, orthorhombic, monoclinic and triclinic crystals", *Revs. Mod. Phys.* **64** (1992) 3–49.

[15] N. D. Mermin, "Crystallography without periodicity", *Proceedings of the XIX International Colloquium on Group Theoretical Methods in Physics,* Anales de fisica, Monografias, Eds. M. A. Olmo and M. Santander (CIIEMAT/RSEF, Madrid, 1993) Vol. II, 302–317.

[16] N. D. Mermin and R. Lifshitz, "Bravais Classes for the Simplest Incommensurate Crystal Phases", *Acta Cryst.* A**48** (1992) 515–532.

[17] N. D. Mermin, D. S. Rokhsar, and D. C. Wright, "Beware of 46-fold symmetry: The classification of two-dimensional quasicrystallographic lattices", *Phys. Rev. Lett.* **58** (1987) 2099–2101.

[18] D. A. Rabson, T.-L. Ho, and N. D. Mermin, "Aperiodic tilings with nonsymmorphic space groups $p2^j gm$", *Acta Cryst.* A**44** (1988) 678–688.

[19] D. A. Rabson, N. D. Mermin, D. S. Rokhsar, and D. C. Wright, "The space groups of axial crystals and quasicrystals", *Revs. Mod. Phys.* **63** (1991) 699–733.

[20] D. S. Rokhsar, N. D. Mermin, and D. C. Wright, "Rudimentary crystallography: The icosahedral and decagonal reciprocal lattices", *Phys. Rev* **B35** (1987) 5487–5495.

[21] D. S. Rokhsar, D. C. Wright, and N. D. Mermin, "The two-dimensional quasicrystallographic space groups with rotational symmetries less than 23-fold", *Acta Cryst.* A**44** (1988) 197–211.

[22] D. S. Rokhsar, D. C. Wright, and N. D. Mermin, "Scale equivalence of quasicrystallographic space groups", *Phys. Rev.* B**37** (1988) 8145–8149.

[23] H. Selke, U. Vogg, and P. L. Ryder, "New quasiperiodic phase in $Al_{85}Cr_{15}$", *Phys. Stat. Sol. (a)* **141** (1994) 31–41.

[24] M. Senechal, "Crystalline symmetries: an informal mathematical introduction", (Adam Hilger, Bristol, 1990).

[25] D. Shechtman, I. Blech, D. Gratias, and J. W. Cahn, "Metallic phase with long-range orientational order and no translational symmetry", *Phys. Rev. Lett.* **53** (1984) 1951–1953.

[26] S. van Smaalen, "Incommensurate crystal structures", *Cryst. Rev.* **4** (1995) 79–202.

[27] S. van Smaalen, "Symmetry of composite crystals", *Phys. Rev.* B**43** (1991) 11330–11341.

[28] S. van Smaalen, "Superspace description of incommensurate intergrowth compounds and the application to inorganic misfit layer compounds", *Materials Science Forum* **100** & **101** (1992) 173–222.

[29] P. M. de Wolff, T. Janssen, and A. Janner, "The superspace groups for incommensurate crystal structures with a one-dimensional modulation", *Acta Cryst.* A**37** (1981) 625–636.

[30] A. Yamamoto, "Unified setting and symbols of superspace groups for composite crystals", *Acta Cryst.* A**48** (1992) 476–483; and "Determination of composite crystal structures and superspace groups", *Acta Cryst.* A**49** (1993) 831–846.

[31] A. Yamamoto, T. Janssen, A. Janner, and P. M. de Wolff, "A note on the superspace groups for one-dimensionally modulated structures", *Acta Cryst.* A**41** (1985) 528–530.

[32] International Union of Crystallography, "Report of the Executive Committee for 1991", *Acta Cryst.* **A48** (1992) 922–946.

Chapter 2

Bravais Classes for the Simplest Reducible Incommensurate Lattices

2.1 Introduction

In this chapter we apply Fourier-space crystallography to an enumeration of the Bravais classes of the simplest reducible incommensurate lattices: all rank-6 cubic and tetrahedral lattices and all rank-4 lattices with any of the other crystallographic point groups. This in fact covers all 3-dimensional rank-4 lattices because the minimal rank required for a lattice to be invariant under any other point group is greater than 4. Such lattices can describe the symmetry of incommensurately modulated crystals or composite crystals, as well as arbitrary quasiperiodic crystals with no obvious sublattice of main reflections.

A classification of all of these lattices has already been carried out using the superspace approach by Janner, Janssen, and de Wolff[5, henceforth JJdW], but not into Bravais classes as we define them here. The classification scheme of JJdW was designed specificly for the treatment of incommensurately modulated crystals long before the discovery of the first AlMn quasicrystal. It requires the existence of a rank-3 sublattice of main reflections, associated with the strong Bragg peaks, which plays a special role in the classification. As such, it distinguishes between lattices which contain the same set of 3-dimensional wave vectors but which associate the main reflections with distinct subsets. We consider the JJdW classes (which they unfortunately also call "Bravais classes"), which contain the same sets of wave vectors and differ only in the intensities of the associated Bragg peaks, as different "settings" of a single one of our Bravais classes.

We begin in section 2.2 by giving more precise definitions of "lattice" and "Bravais class", introducing the notions of "reducibility" and "decomposability" with respect to lattices, and discussing the idea of "settings" which emphasize distinct sublattices of main reflections. In section 2.3 we introduce the "modular lattice method" and apply it to the enumeration of the Bravais classes, and in section 2.4

to the enumeration of the distinct settings of each of the Bravais classes. All the results of the enumeration, carried out in this chapter, are summarized in Tables 2.1 and 2.2 on pages 38 and 39.

2.2 Preliminary Definitions and Remarks

2.2.1 The Lattice

Our formulation of crystallography in 3-dimensional Fourier space, like the superspace approach, applies to all materials whose diffraction patterns can be described in terms of a set of sharp Bragg peaks — *i.e.* to periodic or quasiperiodic materials. The fundamental concept in this formulation is a set L of 3-dimensional wave vectors which is a simple extension of the set of wave vectors that the familiar Laue rules associate with each of the experimentally observed Bragg peaks. We define L to be the set of all integral linear combinations of wave vectors determined by the Bragg peaks. Alternatively (and equivalently) L can be viewed as the smallest set of vectors which is closed under subtraction (and hence addition), which contains all the wave vectors determined by the diffraction pattern. We call the set L of 3-dimensional wave vectors a *lattice*.

We are interested in lattices L whose 3-dimensional vectors can be represented as integral linear combinations of no fewer than D *generating vectors* which are linearly independent over the integers. The number D is called the *rank* or indexing dimension of L. For any lattice L it is always possible to find a set of D *primitive generating vectors*, such that L contains *all* integral linear combinations of these D vectors.[1]

A crystal is *periodic* if and only if the rank of its lattice is equal to the physical dimension d. Only then is L a conventional "reciprocal lattice" related in the familiar way to a lattice of real-space translations under which the periodic crystal is invariant. For *quasiperiodic* crystals $D > d$, and we refer to the set of 3-dimensional wave vectors as an *incommensurate lattice*. Incommensurate lattices have the property that any wave vector in the lattice will have other wave vectors arbitrarily close to it. This does not mean that measured diffraction patterns can display this highly mathematical property, but merely that for an ideal material more and more peaks will be revealed as the experimental resolution improves. This presents no more of a practical problem for the determination of the lattice than does the fact that only a finite number of peaks are observed in diffraction measurements of ordinary periodic crystals. In both cases it is necessary to determine only a finite number of wave vectors (at least D, of course) to determine the entire infinite lattice L.

[1] A lattice L which is generated non-primitively by a set of D integrally-independent vectors is a sublattice of the lattice which is generated by taking all integral linear combinations of the same D vectors. The statement that L can be generated by a set of D primitive generators follows from a theorem that any submodule of a free $\mathbf{Z}$-module is free (see Hartley and Hawkes[4, Theorem 7.8]).

The point group of the lattice – its holohedry – is the set of proper and improper rotations applied about the origin of Fourier space which leave the lattice invariant. We consider only finite subgroups of $O(3)$ and require that they contain the inversion because any lattice contains the negative of each of its vectors.

Two remarks about nomenclature:

1. We shall always use the term "lattice" to refer to the set L of 3-dimensional wave vectors and not to any direct lattice of translations in ordinary (or higher-dimensional) real space. We use this nomenclature because it is the obvious generalization to quasiperiodic materials of the "reciprocal lattice" of periodic materials. In the quasiperiodic case there is no dual direct lattice of translations in real 3-dimensional space, and therefore no ambiguity arises from omitting the adjective "reciprocal". When we wish to emphasize that the lattice L is in Fourier space we may refer to it as a reciprocal lattice, but we stress that only in the rank-3 case is L dual to a lattice of translations in 3-dimensional space.

2. The abstract algebraic structure of what we define as a lattice is called by mathematicians a $\mathbb{Z}$-*module* and will be briefly discussed in section 2.2.3 below. Only when the rank of a module is equal to the number of spatial dimensions do mathematicians call it a lattice. We find it awkward to impose upon physicists such a nomenclature and therefore refrain from doing so. In the superspace approach one introduces, in addition to the set of 3-dimensional wave vectors which form a rank-D $\mathbb{Z}$-module, a reciprocal lattice of D-dimensional wave vectors, which is an extension of the $\mathbb{Z}$-module to a higher dimension and is dual to a direct lattice of D-dimensional translations. Under such circumstances, where one must distinguish between the two sets of wave vectors, one must use both terms. In the Fourier-space approach this confusion does not arise because there is only a single set of wave vectors forming the 3-dimensional rank-D lattice.

2.2.2 The Bravais Class

Our classification scheme rests on the following definition of Bravais class:

> *Two rank-D lattices with point group G are in the same Bravais class if there is a sequence of rank-D lattices all with point group G that interpolates between them.*

We shall refer to any particular lattice in a given Bravais class as a "representative" or a "member" of that class.

Several comments are required:

1. By interpolating sequence, we mean a sequence whose adjacent members can be taken as close together as one pleases. There are two technical reasons why we cannot simply interpolate via a continuous family of lattices: (a) Isolated members of a continuous family of lattices might necessarily be more symmetric. In the periodic case, for example, it may be impossible continuously to deform one rank-3

rhombohedral lattice into another while retaining rhombohedral symmetry without momentarily passing through at least one intermediate cubic lattice. (b) As one continuously deforms one lattice in a rank-D Bravais class into another, one will in general be unable to avoid passing through intermediate lattices where certain irrational ratios happen to be rational. Such intermediate lattices will have a lower rank. An interpolating sequence, however, can avoid the rational values.

2. Worries about how properly to define proximity of members in view of the fact that no lattice vector of a quasiperiodic structure has a neighborhood free of other vectors can be circumvented by taking the lattice to be entirely specified by a finite set of integrally independent generating vectors (and an indexing convention, if the generators are not primitive), and defining proximity of lattices by the proximity of their generating vectors. One then asks whether there is an interpolating sequence that takes *an arbitrarily chosen* set of generating vectors of one lattice into generators of the other lattice.

3. It is central to our classification scheme that the Bravais class of a material is entirely determined by the set of three-dimensional wave vectors L; the relative intensities of the Bragg peaks associated with the wave vectors giving rise to L are irrelevant for this purpose. Since the Fourier expansion of the density of a material with a lattice L is given by a set of Fourier coefficients $\rho(\mathbf{k})$ which are non-zero on a set of wave vectors $\mathbf{k}$ whose integral linear combinations give L, any two densities with the same Bravais class can be interpolated into one another without ever leaving that Bravais class. There is thus no way to make a sharp distinction between densities associated with the same Bravais class, as a further subdivision of Bravais classes based on Bragg peak intensities would require. We do not address here the more difficult question of whether two densities in the same Bravais class that describe impenetrable spheres at a specified set of real-space positions can be deformed into each other without leaving the Bravais class. But a fundamental classification scheme ought to be broad enough to encompass materials (for example certain liquid crystals, or incommensurate modulations of a continuous electronic charge density) for which such conceivable obstructions to continuous deformation are irrelevant.

2.2.3 Lattices as Integral Representations of the Point Group

A $\mathbb{Z}$-module, in our context, is a set of vectors which contains any integral linear combination of its members and which carries an integral representation of some group.[2] In our case the vectors are 3-dimensional wave vectors and the group is the point group of the lattice. The representation is just the set of $D \times D$ integral matrices which describe the action of the elements of the group on a chosen set of D generators for the module. The module gives infinitely many representations

[2]The precise and more general definition of module is much more abstract and out of the scope of our discussion.

in this way (one for every choice of basis) but they are all equivalent, related by a basis transformation. The module is therefore identified with the representation that it carries. One talks about reducibility and decomposability of $\mathbb{Z}$-modules — two notions that we shall adopt for our treatment of lattices — defined in terms of the reducibility and decomposability of the corresponding integral representation. The definitions given below[3] make precise the following notions: if a lattice L can be written as a sum of two sublattices $L_1 + L_2$ such that L_1 is independently invariant under the point group then L is called reducible; if L_2 is also independently invariant under the point group then L is called decomposable.

A rank-D lattice is *reducible* if there is a basis (a set of lattice generating vectors) in terms of which all the integral matrices representing the action of the point group elements on the lattice have the following form:

$$\begin{pmatrix} \mathcal{M}_1 & \mathcal{M}_3 \\ \mathcal{M}_4 & \mathcal{M}_2 \end{pmatrix}, \qquad \mathcal{M}_3 = 0, \tag{2.1}$$

where $\mathcal{M}_1$ is a $D_1 \times D_1$ matrix, $\mathcal{M}_2$ is a $D_2 \times D_2$ matrix, both D_1 and D_2 are non-zero, and $D_1 + D_2 = D$. The first D_1 basis vectors generate a sublattice of rank D_1 which is independently invariant under the point group. This is exactly the property of the sublattice of main reflections which appears in the case of modulated crystals. The reducibility of a lattice may be non-unique, making it possible for example, to have two distinct rank-3 sublattices of main reflections, belonging to different rank-3 Bravais classes, in a single rank-4 lattice.

A rank-D lattice is *decomposable* (also called fully reducible) if there is a basis in terms of which all the integral matrices representing the action of the point group elements on the lattice have the following form:

$$\begin{pmatrix} \mathcal{M}_1 & 0 \\ 0 & \mathcal{M}_2 \end{pmatrix}, \tag{2.2}$$

where $\mathcal{M}_1$ is a $D_1 \times D_1$ matrix, $\mathcal{M}_2$ is a $D_2 \times D_2$ matrix, both D_1 and D_2 are non-zero, and $D_1 + D_2 = D$. Every decomposable lattice is reducible but the converse is not true in general. A matrix of the form (2.2) is said to be a *direct sum* of the matrices $\mathcal{M}_1$ and $\mathcal{M}_2$, and the rank-D lattice L is the sum of a rank-D_1 lattice L_1 and a rank-D_2 lattice L_2, each independently invariant under the action of the point group. The lattice $L = L_1 + L_2$ consists of sums of all pairs of vectors from L_1 and L_2, which is the same as saying that it is the set of all the integral linear combinations of vectors in the union of L_1 and L_2.

A Bravais class is said to be reducible (decomposable) if its members are reducible (decomposable). A lattice which is not reducible is called *irreducible* and a lattice which is not decomposable is called *indecomposable*. The three rank-3 cubic Bravais classes for periodic crystals (sc, fcc, and bcc) are all irreducible. The

[3]Definitions like these may be found in many books, see for example Opechowski[10, page 132].

primitive rank-3 tetragonal and the rank-3 hexagonal Bravais classes are both decomposable into a rank-1 lattice along the axis of 4-fold or 6-fold rotation and a rank-2 lattice in the horizontal plane perpendicular to the axis of rotation. The rank-3 trigonal and the centered tetragonal Bravais classes are both indecomposable but they are reducible, containing a rank-2 invariant sublattice in the horizontal plane.

We shall find here that all the rank-4 lattices describing 3-dimensional quasiperiodic crystals as well as all the rank-6 lattices, invariant under the full cubic point group, are decomposable. The only Bravais classes, enumerated here, that are indecomposable, yet reducible, are the three Bravais classes of rank-6 tetrahedral lattices (invariant under the tetrahedral group $m\bar{3}$ but not under the full cubic group $m\bar{3}m$). In Chapter 4 we shall show that all hexagonal and trigonal lattices of arbitrary finite rank are decomposable into lattices of ranks 1, 2, and 3. This property of the hexagonal and trigonal lattices greatly simplifies their enumeration as well as the full classification of space groups.

We say that a rank-4 Bravais class is a trivial extension of a rank-3 Bravais class, or simply trivial, if it is 3+1 decomposable, that is decomposable into a sum of a rank-3 lattice and a rank-1 lattice (the rank-3 lattice may be further decomposable). Only two of the sixteen rank-4 Bravais classes, enumerated here, are non-trivial: a class labeled M in the monoclinic system and a class labeled O in the orthorhombic system. These two Bravais classes are 2+2 decomposable.

2.2.4 Lattices of Main Reflections as Settings of the Bravais Classes

When an observed diffraction pattern exhibits one or more obvious sublattices of main reflections, as in the cases of incommensurately modulated crystals and composite crystals, a finer classification is required which distinguishes between two structures with lattices in the same Bravais class but with distinct sublattices of main reflections. One can have, as will be shown below, rank-4 crystals with lattices in the orthorhombic O Bravais class which are modulated crystals whose average structure produces a rank-3 orthorhombic I^* sublattice of main reflections; modulated crystals whose average structure produces a rank-3 C-centered orthorhombic lattice of main reflections; and even, as in the case of $(LaS)_{1.14}NbS_2$, composite crystals where both sublattices of main reflections are present[4] All these structures should clearly be distinguished.

Since these cases are abundant, especially on the lattices enumerated in this chapter, it is important to have this finer classification, even though it is based on relative Bragg peak intensities, beyond what symmetry alone requires. This does not mean that considerations regarding Bragg peak intensities (other than the requirement, imposed by the definition of phase function (1.4), that peaks related by the point group symmetry have the same intensity) must be incorporated into the

[4]See Van Smaalen[12] and Lifshitz and Mermin[7].

symmetry based classification. It only means that after the symmetry classification — which is general and applicable to any quasiperiodic crystal — is completed, one should then in make the finer distinctions.

When a diffraction pattern does display an obvious sublattice of main reflections, it can also be of help in identifying its rank-D Bravais class, since lattices in the rank-D Bravais class characterizing the material must be appropriately reducible. Noting this constraint can reduce the number of candidates for the full rank-D Bravais class. In the orthorhombic system, for example, the *only* rank-4 lattices which contain rank-3 sublattices from both the rank-3 I^* Bravais class and the rank-3 C-centered Bravais class are those which belong to the rank-4 O Bravais class.

Identifying a particular sublattice of main reflection is equivalent to putting the lattice in the appropriate reducible form. This is achieved by choosing a set of lattice generating vectors for the full lattice, of which the first three generate the invariant sublattice of main reflections. We call any particular choice of generating vectors a *setting* of the lattice, in much the same way as the rank-3 A-, B-, and C-centered orthorhombic lattices are different settings of lattices belonging to the same Bravais class.

We say that two lattices belonging to the same Bravais class are in the same setting (in the sense described above with regards to a sublattice of main reflections) if the interpolating sequence that takes one into the other also takes the sublattice of main reflections of the one into that of the other. Defined in this way, our settings are equivalent to the "Bravais classes for incommensurately modulated crystals" which are the outcome of the JJdW classification. Thus, two JJdW Bravais classes may correspond to (two settings of) a single one of our Bravais classes. In the Bravais classes enumerated in this chapter it is always the case that a setting can be characterized simply by specifying the Rank-3 Bravais class of the sublattice of main reflections. We shall see in Chapter 4 that in general one can have two distinct settings in which the sublattices of main reflections belong to the same rank-3 Bravais class.

2.3 Computation of the Bravais Classes.

2.3.1 The Modular Lattice Method

We derive below the rank-4 (or, in the cubic case, rank-6) Bravais classes for each of the seven crystal systems, by examining the structure of lattices of 3-dimensional wave vectors L that can be indexed by 4 (or 6) integrally independent vectors, and are invariant under the operations of a point group G belonging to the crystal system. We call the method that we use here "the modular lattice method". This method was used by Rokhsar, Mermin, and Wright[11] as part of the enumeration of the three rank-6 icosahedral Bravais classes. We use the method here for most of the

cases except for the triclinic and (planar) monoclinic systems where the symmetry is so low that a more direct approach is preferable. The aim of this chapter is to produce the promised enumeration but, equally important, to properly introduce the method so it may be used again in the future. The general strategy is as follows:

(*i*) We identify a particularly simple Bravais class B_P, and show that any rank-D lattice L in the crystal system contains a rank-D sublattice L_P that is in B_P. We call the class B_P (P for "primitive") because, as we shall see, in many cases it contains the primitive lattices which have no centerings.

(*ii*) We note that the full lattice L can be constructed by adding each of the vectors in L_P to every one of the vectors in a finite subset L_0 of L. We call L_0 the "modular lattice" of L, adding the phrase "modulo L_P" if we wish to be absolutely explicit, because L_0 is itself closed under addition and subtraction if these operations are defined modulo the vectors of L_P. From a group theoretic perspective, if one views the lattice L as an abelian group and the lattice L_P as its subgroup, then the vectors in L_0 correspond to the cosets of L_P in L and the modular lattice L_0 is the quotient group L/L_P.

(*iii*) We note that since the sublattices L_P for different L are all in the same Bravais class, two lattices L will be in the same Bravais class if their modular lattices L_0 are in the same Bravais class — *i.e.* if there is a family of modular lattices that interpolates between them.

(*iv*) Because the modular lattices contain only a small number of points (at most 16 in any of the rank-4 cases and 64 in the rank-6 cubic case) one can catalogue their Bravais classes by an exhaustive enumeration of the possibilities.

(*v*) For given L_P, one checks for a further (entirely routine) equivalence of Bravais classes of lattices L associated with distinct modular lattices L_0 when there are different but equivalent ways to represent L in terms of an L_P and a modular L_0.

In preparation for the analysis that follows, it may help to illustrate these concepts with some familiar crystallographic examples.

Example 1: Rank-3 Bravais classes in the cubic system.

Every lattice in the cubic system contains a simple cubic sublattice L_P in the primitive (P) Bravais class. If we represent L_P as the set of vectors all of whose cartesian components are even integers, then the modular lattices L_0 are sets of vectors each of whose components can be either 1 or 0 — *i.e.* the components are integers modulo 2. The cubic rank-3 Bravais classes are associated with the following modular lattices L_0:

(a) *P lattice.* L_0 can contain only the vector 0 (in which case we have a P lattice (with lattice constant 2). A second choice for L_0 contains all eight possible vectors (in which case we have a P lattice again (with lattice constant 1). This is an example of the routine equivalence one has to watch out for in step (v) above. The formal basis for this (informally obvious) equivalence is that the lattice L with L_0 consisting of all 8 vectors can be interpolated into the one with the L_0 containing only the 0 vector by a symmetry preserving isotropic expansion by a factor of 2. When alternative ways arise of representing a Bravais class by a modular lattice L_0 we shall always chose the L_0 with the smallest number of vectors.

(b) *I^* (F) lattice.*[5] L_0 consists uniquely of the two vectors 000 and 111. Note that if arithmetic is done modulo 2, these two vectors do indeed constitute a lattice, because one gets no further vectors by taking any integral linear combinations of them. Note that the modular lattice L_0 can be viewed geometrically as the conventional two site "basis" when one choses to represent the I^* lattice as simple cubic with two sites per unit cell.

(c) *F^* (I) lattice.* L_0 consists uniquely of the four vectors 000, 110, 101, and 011. Note again that this set contains all integral linear combinations (modulo 2) of its four vectors, and can be viewed geometrically as the conventional four site "basis" employed when one represents the F^* lattice as simple cubic with four sites per unit cell.

Example 2: Rank-3 Bravais classes in the orthorhombic system.

Every rank-3 lattice in the orthorhombic system contains a simple orthorhombic sublattice L_P in the primitive (P) Bravais class. If we represent L_P as the set of vectors whose cartesian components are even integral multiples of three unrelated lengths a, b, and c, then the modular lattices L_0 contain vectors whose components are multiples of these three lengths by either 1 or 0. If we denote the vector $n_1a\mathbf{x} + n_2b\mathbf{y} + n_3c\mathbf{z}$ by $n_1n_2n_3$ then we can describe the modular lattices L_0 associated with the four orthorhombic Bravais classes as follows:

(a) *I^* (F) and F^* (I) lattices.* As in the cubic case, in the I^* Bravais class L_0 can only contain the two vectors 000 and 111, and in the F^* class, only the four vectors 000, 110, 101, and 011.

(b) *P lattice.* Here there are 8 routinely equivalent L_0 (in the sense of step *(v)* above). Taking L_0 to contain only 0 gives the P–lattice with lattice constants $2a$, $2b$, and $2c$. We get the P lattice with the lattice constant along $\mathbf{x}$ reduced from $2a$ to a, by taking L_0 to contain 000 and 100, and similarly for $\mathbf{y}$ and $\mathbf{z}$. We can get the P lattice with the lattice constants along both $\mathbf{y}$ and $\mathbf{z}$ reduced from $2b$ and $2c$ to b and c by taking L_0 to contain the four vectors 000, 010, 001, and 011 (with two more possibilities arising from cyclic permutations of the axes). And, finally,

[5] We denote lattices according to their centering in Fourier space and use an asterisk as a reminder of that.

as in the cubic case if we take L_0 to contain all 8 points, we get back the original P lattice, uniformly scaled down by a factor of 2.

(c) *C lattice.* If the preferred direction is along $\mathbf{z}$ then the C lattice arises when L_0 contains the two vectors 000, 110, and also (contracted by a factor of 2 along $\mathbf{c}$) when L_0 contains the four vectors 000, 110, 001, and 111. Analogous pairs of modular lattices L_0 give the centered orthorhombic lattice with the preferred direction along $\mathbf{x}$ (often called the A lattice) or $\mathbf{y}$ (B lattice).

These examples should make it clear that the method by which we shall extract the rank-D Bravais classes is nothing more than a formalization of the common practice of viewing the rank-3 Bravais classes in terms of primitive lattices with or without various kinds of centerings, in which we exploit the fact that the centering points must always have a lattice structure modulo the primitive lattice.

In section 2.3.2 we examine those features of orthorhombic and cubic symmetry which lead to the existence of primitive sublattices L_P. (We later apply minor variations of the same arguments to the remaining crystal systems.) We then extract the rank-4 orthorhombic Bravais classes in section 2.3.3, the rank-6 cubic Bravais classes in section 2.3.4, the rank-4 tetragonal and axial monoclinic Bravais classes in section 2.3.5, the rank-4 hexagonal and trigonal Bravais classes in section 2.3.6, and the triclinic and planar monoclinic Bravais classes in section 2.3.7.

The Bravais classes enumerated in this chapter are summarized in Table 2.1 and Table 2.2.

2.3.2 Features Common to the Orthorhombic and Cubic Cases

Since lattices are closed under subtraction, any lattice contains the negative of each of its vectors, and the point group G of any rank-D lattice must contain the inversion i. As a result the point group of a rank-D lattice in the orthorhombic system is necessarily the full orthorhombic group mmm; the cubic system, however, admits the possibility (not realized in the rank-3 case) of rank-D lattices with either the full cubic point groups $m\bar{3}m$, or the smaller tetrahedral point group $m\bar{3}$. Lattices with any of these three point groups will have among their point-group symmetries three mutually perpendicular axes of 2-fold symmetry, $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$.

Any lattice with three such axes contains the sum of any of its vectors with the image of that vector under any of the 2-fold rotations — *i.e.* it contains twice the projection of any of its vectors on each of the 2-fold axes. The subset L_c of L consisting of twice the projections on the c-axis, $2P_c\mathbf{k}$, of all $\mathbf{k}$ in L is a rank-D_c lattice[6] and as such it can be *primitively* indexed by D_c of its vectors; *i.e.* one can choose D_c integrally independent incommensurate length scales $k_1, \ldots k_{D_c}$ so that L_c consists of *all* integral linear combinations of the vectors $k_1\mathbf{c}, \ldots k_{D_c}\mathbf{c}$. Similar remarks hold for L_a and L_b, with $D = D_a + D_b + D_c$.

[6]For the moment we let D_c be general; we will soon specialize to the case of interest, $D_c = 2$, $D_a = D_b = 1$ (or, in the cubic case, $D_a = D_b = D_c = 2$).

The fact that the indexing can be taken to be primitive is a special case of the fact that any vector space over the integers of dimension D_c can be expressed as the set of *all* integral linear combinations of a suitably chosen basis of D_c vectors. Note that two lattices that differ only in the values of the incommensurate length scales $k_1 \ldots k_{D_c}$ that characterize the primitive basis for the sublattice L_c are in the same Bravais class (for essentially the same reasons that any two triclinic rank-3 lattices are in the same class). In the cubic (as opposed to the orthorhombic case) one can and should always associate the same set of length scales with each of the three sublattices L_a, L_b, and L_c.

Because twice the projection of any vector in L on the axes **a**, **b**, and **c** is in the sublattices L_a, L_b, and L_c, it follows that any vector of L can be expressed as an integral or half-integral linear combination of the vectors $k_1\mathbf{c}, \ldots k_{D_c}\mathbf{c}$ and the analogous two sets for the axes **a** and **b**, and that *all* integral (but not necessarily all half-integral) linear combinations are present. It is convenient to restate this conclusion in the form it assumes when the axes are rescaled by a factor of 2:

Any cubic or orthorhombic rank-D lattice can be expressed as a set of integral linear combinations of integrally independent vectors along three orthogonal directions, with an even sublattice[7] L_P *that is primitively generated.* Note that this generalizes to the rank-D case the form of L_P we described in the crystallographic examples above, and explains why L_P arises naturally with even indexing.

The cubic and orthorhombic rank-D lattices can therefore be viewed as the translations through all vectors of the primitive even sublattice L_P, of the set L_0 of vectors indexed only by 0's or 1's. The modular lattice L_0 is closed under subtraction when arithmetic is performed on its components modulo 2, as an immediate consequence of the closure of the full lattice L under ordinary subtraction. Since the sublattices L_P of any two lattices L with the same G and same D_a, D_b, and D_c are clearly in the same Bravais class, classifying distinct lattices L by Bravais class, reduces to classifying the distinct modular lattices L_0. The modular lattices inherit from the full lattice L the property that they belong to the same Bravais class if they differ only in the choice of primitive vectors along the axes.

At this point we specialize to the cases of rank-4 orthorhombic and rank-6 cubic lattices.

2.3.3 The Orthorhombic Case

We take the two incommensurate length scales k and k', in terms of which the even sublattice is primitively generated, to be associated with the axis **c**, and index the projections of lattice vectors along the c–axis by $n_3k + n_3'k'$. Note that two lattices L (or two modular lattices L_0) that differ only in the interchange of n_3 and n_3' for all their vectors belong to the same Bravais class, since this merely corresponds to interchanging the roles of $2k$ and $2k'$ as primitive generators of L_c. More generally, a

[7] By the even sublattice, we mean the sublattice of vectors all of whose indices are even.

new Bravais class does not result from a transformation of all the n_3 and n_3' induced by a replacement of $2k$ and $2k'$ by any of their linear combinations with integral coefficients that continue to generate L_c primitively (characterized by matrices with determinant ± 1), since this merely changes the basis in terms of which the lattice L is described, or interchanges two lattices within the same Bravais class. The effect of such a linear transformation on vectors of the modular lattice L_0 is either to interchange n_3 with n_3', to replace either n_3 or n_3' with $n_3 + n_3'$ (keeping the other index unchanged), or to combine the interchange and the replacement. Thus the Bravais class is unchanged by subjecting the two indices n_3 and n_3' of every vector in the modular lattice to any of the transformations:

$$n_3, n_3' \rightarrow \begin{array}{l} n_3, n_3 + n_3' \\ n_3 + n_3', n_3' \\ n_3', n_3 \\ n_3 + n_3', n_3 \\ n_3', n_3 + n_3' \end{array} . \tag{2.3}$$

We use the term "reindexing" to refer to this freedom to replace the indices specifying L_0 by any of these linear combinations, without altering the Bravais class. If two rank-4 orthorhombic Bravais classes are characterized by modular lattices L_0 that differ only by a reindexing transformation, then the two classes contain identical sets of lattices and must be identified. Keeping these equivalences in mind, we now enumerate the distinct modular lattices L_0 and hence the distinct Bravais classes of orthorhombic rank-4 lattices.

Evidently there are five trivial rank-4 orthorhombic Bravais classes, associated with the four ordinary orthorhombic rank-3 Bravais classes. (The centered orthorhombic rank-3 class gives rise to two rank-4 classes, since it alone has a preferred direction among **a**, **b**, and **c**, which can either be along (C lattice) or orthogonal (A or B lattice) to the direction of the axis containing the two incommensurate wave vectors.) We call these lattices $P+1$, F^*+1 (or $I+1$), I^*+1 (or $F+1$), $C+1$, and $A+1$ (or $(B+1)$).[8] We now show that in addition there is just a single non-trivial Bravais class of orthorhombic rank-4 lattices.

Note that a lattice L belongs to a trivial Bravais class if and only if the associated modular lattice L_0 does. A Bravais class of modular lattices is trivial if and only if it contains sublattices in which all vectors are of the form

$$n_1 n_2 n_3 0, \tag{2.4}$$

or in which every vector appears as a member of a pair of vectors differing only in their fourth components,[9] so that L_0 is the sum of a lattice of the form (2.4) with the lattice [0000 0001].

[8] As noted earlier, the asterisk is to emphasize that the centering is specified in Fourier space.

[9] The second case can be converted back to the first by rescaling the c-axis by a factor of 2.

It is convenient[10] to separate out the 2-dimensional sublattice L_0^{ab} of L_0 spanned by **a** and **b**, which contains all modulo-2 vectors of the form n_1n_200. Because we are doing arithmetic modulo 2, there are just five possibilities[11] for L_0^{ab}:

$$\begin{array}{ccccc} & & [0000]; & & \\ [0000 & 1000]; & [0000 & 0100]; & [0000 & 1100]; \\ & & [0000 & 1000 & 0100 & 1100]. \end{array} \tag{2.5}$$

Consider next the set of vectors in L_0 whose third and fourth components are 1,0. Because L_0 is a lattice, one easily establishes that if this set is not empty, it is given by adding to every vector in L_0^{ab} a vector of the form $n_1'n_2'10$, where $n_1'n_2'00$ (which is only determined to within an additive vector from L_0^{ab}) can be taken to be either 0000 or a vector not in L_0^{ab}. In the same way if L_0 contains any vectors whose third and fourth components are 0,1, then the set of them is just L_0^{ab} shifted by a vector $n_1''n_2''01$, and those, if any, with third and fourth components 1,1, are L_0^{ab} shifted by a vector $n_1'''n_2'''11$. If two of the types are present then the third (which contains their sums) must also be. If all three types are present then we can pick the shift vectors to satisfy

$$n_1'n_2'10 + n_1''n_2''01 \equiv_2 n_1'''n_2'''11, \tag{2.6}$$

where "$\equiv_2$" indicates equality modulo 2.

The general form of L_0 is thus:

(a) L_0^{ab} alone.

(b) L_0^{ab} augmented by shifting every vector in L_0^{ab} by a single vector of one of the three types

$$n_1'n_2'10 \quad n_1''n_2''01 \quad n_1'''n_2'''11. \tag{2.7}$$

Because of the invariance of the Bravais class under the reindexing transformations (2.3), the shift can always be represented by the first type.

(c) L_0^{ab} augmented by shifting every vector in L_0^{ab} by a single vector of every one of the three types.

Cases (a) and (b) clearly yield only trivial rank-4 lattices, so non–trivial rank-4 lattices can be only of type (c), with the shift vectors related by (2.6). If n_1'' and n_2'' are zero, so that L_0^{ab} contains the vector[12] 0001, then the rank-4 lattice is again trivial. This leaves only the case in which the first two components of every one of the vectors (2.7) are not both zero, and all three pairs of components are different. The only possibility is thus $n_1'n_2' = 10$, $n_1''n_2'' = 01$, and $n_1'''n_2''' = 11$, or permutations

[10] From this point on the analysis makes no further use of the orthogonality of the axes **a** and **b**, and therefore, as we shall note in section 2.3.5, applies equally well to the axial monoclinic case.

[11] We specify the vector $n_1\mathbf{a} + n_2\mathbf{b} + n_3k\mathbf{c} + n_3'k'\mathbf{c}$ by listing $n_1n_2n_3n_3'$, which we separate by commas only when it would be confusing not to do so. When we wish to emphasize that a set of vectors constitutes a modular lattice we enclose the set in square brackets.

[12] Because of reindexing equivalence, this case generates the same Bravais class as those given by chosing the primed or triple primed pair to vanish.

of these assignments, which yield the same Bravais classes, since they differ only by a reindexing transformation. Since none of these three pairs of indices can be in L_0^{ab}, that lattice can contain only the point 00, and we arrive at a modular sublattice consisting of just four points:

$$L_0 = [0000 \;\; 1010 \;\; 0101 \;\; 1111]. \tag{2.8}$$

Equation (2.8) specifies the modular sublattice of the only non-trivial orthorhombic rank-4 Bravais class, which we call O. The fact that it is not a trivial extension of a rank-3 lattice follows from the fact that none of the five reindexing transformations (2.3) performed on the last two indices of the vectors in (2.8) can reduce L_0 to the trivial form

$$[0000 \;\; n_1n_2n_30 \;\; 0001 \;\; n_1n_2n_31] \tag{2.9}$$

or a form in which all four fourth components are 0. On the other hand one can express the lattice as a direct sum of two rank-2 lattices

$$L_0 = [0000 \;\; 1010] + [0000 \;\; 0101] \; . \tag{2.10}$$

These are easily recognized as two 2-dimensional centered rectangular lattices one in the *ac* plane and the other in the *bc* plane.

2.3.4 The rank-6 Cubic and Tetrahedral Case

If a lattice has cubic symmetry its point group G must contain in addition to the 2-fold axes **a**, **b**, and **c**(now specified by vectors of the same lengths), a 3-fold axis, which we can take to be associated with cyclic permutations of **a**, **b**, and **c**. If G contains *all* permutations it is the full cubic group $m\bar{3}m$; if it contains only cyclic permutations it is the tetrahedral subgroup $m\bar{3}$. As it happens all ordinary rank-3 lattices with cubic symmetry always have $G = m\bar{3}m$ but some rank-6 lattices may also have the lower (tetrahedral) symmetry.

The 3-fold axis requires that the projections of the lattice vectors on each of the three 2-fold axes can be characterized by the same sets of incommensurate lengths. The simplest case is that of rank 6 where there is a pair of such lengths, and a vector in L has the general form

$$(n_1k + n_1'k')\mathbf{a} + (n_2k + n_2'k')\mathbf{b} + (n_3k + n_3'k')\mathbf{c}, \tag{2.11}$$

which we shall sometimes find it more convenient to write in the alternative form

$$(n_1n_2n_3)k + (n_1'n_2'n_3')k', \tag{2.12}$$

or, suppressing explicit reference to the two length scales, in 6–vector form

$$n_1n_2n_3, \;\; n_1'n_2'n_3', \tag{2.13}$$

or, suppressing reference to individual components, in the vector forms

$$k\mathbf{n} + k'\mathbf{n}' \tag{2.14}$$

or

$$\mathbf{n}, \mathbf{n}'. \tag{2.15}$$

When it is convenient to focus on the three components rather than the two length scales, we shall use Greek letters to indicate numbers of the form $nk + n'k'$, and write vectors in L as

$$\alpha\beta\gamma; \quad \alpha = n_1 k + n_1' k', \ \beta = n_2 k + n_2' k', \ \gamma = n_3 k + n_3' k'. \tag{2.16}$$

Note that all of these forms also describe the modular lattice, provided the n_i and n_i' are all restricted to the values 0 or 1 and vector arithmetic is performed modulo 2.

The freedom to chose a primitive basis for the rank-2 sublattices on the axes now leads to the identification of Bravais classes whose modular lattices differ only by the vector generalization of the reindexing transformations (2.3) applied to every point:

$$\begin{array}{rcl} & & \mathbf{n},\ \mathbf{n}+\mathbf{n}' \\ & & \mathbf{n}+\mathbf{n}',\ \mathbf{n}' \\ \mathbf{n},\ \mathbf{n}' & \rightarrow & \mathbf{n}',\ \mathbf{n} \\ & & \mathbf{n}+\mathbf{n}',\ \mathbf{n} \\ & & \mathbf{n}',\ \mathbf{n}+\mathbf{n}'. \end{array} \tag{2.17}$$

Evidently there are six decomposable Bravais classes, given by the six distinct sums of ordinary rank-3 cubic P, I^* (F), or F^* (I) lattices. We shall show that there are, in addition, just three indecomposable rank-6 Bravais classes in the cubic system each with the tetrahedral point group $m\bar{3}$. We note that the three Bravais classes of icosahedral quasicrystals are examples of the three rank-6 tetrahedral Bravais classes, with a special value $\tau = \frac{1}{2}(\sqrt{5}+1)$ for the ratio k/k' that increases the symmetry from tetrahedral to icosahedral.[13]

To extract the distinct Bravais classes of modular lattices L_0 (and hence of rank-6 cubic lattices L) we first show that any modular lattice must be a sum of a rather small number of particular modular sublattices. We then consider all the distinct classes one can arrive at by adding such sublattices.

If $\alpha\beta\gamma$ is an arbitrary vector of an arbitrary rank-6 cubic modular lattice L_0, then cubic symmetry requires L_0 also to contain $\beta\gamma\alpha$ and $\gamma\alpha\beta$; because L_0 is a

[13]This relation is exploited by Dräger, Lifshitz, and Mermin[2,3] who enumerate the space groups for the three rank-6 tetrahedral Bravais classes.

lattice it must, in addition, contain all possible sums modulo 2 of these three. This leads to at most eight members of L_0, implied by the membership in L_0 of $\alpha\beta\gamma$:

$$000;$$

$$\alpha\beta\gamma\,;\quad \beta\gamma\alpha\,;\quad \gamma\alpha\beta\,;$$

$$\alpha+\beta,\ \beta+\gamma,\ \gamma+\alpha\,;\quad \beta+\gamma,\ \gamma+\alpha,\ \alpha+\beta\,;\quad \gamma+\alpha,\ \alpha+\beta,\ \beta+\gamma\,;$$

$$\alpha+\beta+\gamma,\ \alpha+\beta+\gamma,\ \alpha+\beta+\gamma\,. \tag{2.18}$$

No more are implied because further modulo-2 sums of pairs of the eight reduce back to one of them, but there could be fewer, since for particular values of α, β and γ the eight vectors need not all be distinct.

We denote the modular lattice generated in this way from a single vector $\alpha\beta\gamma$ by $\{\alpha, \beta, \gamma\}$. If there are no special relations between α, β, and γ then the modular lattice $\{\alpha, \beta, \gamma\}$ will contain eight distinct elements. It can, however, always be expressed as the sum of the two element lattice

$$[000;\quad \alpha+\beta+\gamma,\ \alpha+\beta+\gamma,\ \alpha+\beta+\gamma] \tag{2.19}$$

and the four element sublattice

$$[000;\quad \alpha+\beta,\ \beta+\gamma,\ \gamma+\alpha\,;\quad \beta+\gamma,\ \gamma+\alpha,\ \alpha+\beta\,;\quad \gamma+\alpha,\ \alpha+\beta,\ \beta+\gamma]. \tag{2.20}$$

The first of these is of the general form

$$\{\eta\,\eta\,\eta\} = [000\quad \eta\eta\eta]. \tag{2.21}$$

The second has the general form

$$\{\phi\,\psi\,\chi\} = [000\quad \phi\psi\chi\quad \psi\chi\phi\quad \chi\phi\psi],\quad \text{with}\quad \phi+\psi+\chi \equiv_2 0. \tag{2.22}$$

We have thus established that every vector in a rank-6 cubic modular lattice L_0 can be taken to be a member of a sublattice that is either of the form (2.21) or (2.22), or the sum of two such sublattices. Consequently L_0 itself can be represented as a sum of (possibly many) sublattices of the forms (2.21) or (2.22).

These sublattices are easily enumerated. Because we work with integers modulo 2, each Greek letter can represent only one of the four numbers

$$0,\quad k,\quad k'\ \text{ or }\ k+k'. \tag{2.23}$$

There are thus just three different two element sublattices of the form (2.21):

$$\{k(111)\},\quad \{k'(111)\},\quad \text{and } \{(k+k')(111)\}, \tag{2.24}$$

which we refer to collectively as I^* lattices, since in the rank-3 cubic case such a modular sublattice generates a lattice that is body centered (I) in reciprocal (*) space. The three lattices L that have a single one of the I^* lattices as their entire modular lattice L_0 are all related by one of the reindexing transformations (2.17) and therefore belong to the same Bravais class. We must nevertheless keep in mind all three forms when building up more elaborate modular lattices by adding together sublattices, since the transformation must be applied to all the vectors in a modular lattice; it cannot be applied independently to each modular sublattice.

To enumerate the distinct forms of the four element modular sublattices (2.22), consider first the case where at least one of ϕ, ψ, or χ is zero. It suffices to consider only one to be zero, since if two are, so is the third and the lattice degenerates to the zero lattice $\{0\}$. The two non–zero numbers must be the same (since their modulo–2 sum is zero) and there are thus just three possible modular lattices,

$$\{k(110)\}, \quad \{k'(110)\}, \quad \{(k+k')(110)\}, \tag{2.25}$$

which we refer to collectively as F^* lattices (since in the cubic rank-3 case such a modular sublattices generates a lattice that is face–centered (F) in reciprocal (*) space. The three lattices L that have a single one of the F^* lattices as their entire modular lattice L_0 are all related by the reindexing transformations (2.17) and therefore belong to the same Bravais class. But as noted above for the I^* lattices, we must keep in mind all three forms when building up more elaborate modular lattices.

To complete the enumeration of the four element lattices (2.22) it remains only to consider the case in which none of ϕ, ψ, or χ are zero. Since we are doing integral arithmetic modulo 2, the vanishing of $\phi+\psi+\chi$ requires each to be the sum of the other two, and and therefore all three must be different if none is to be zero. Since there are only three non–zero choices, we have just two possibilities:

$$\{k, k', k+k'\} \quad \text{or} \quad \{k', k, k+k'\}. \tag{2.26}$$

The two cases differ by a *non*–cyclic permutation of the axes **a**,**b**, and **c** — *i.e.* by an operation of $m\bar{3}m$ not in $m\bar{3}$. One easily verifies that each type is invariant under any of the reindexing transformations (2.17), which only permute the vectors within the lattice. A modular lattice having just one of these as a sublattice will have only tetrahedral symmetry, so we call them T lattices. Since the T lattices are the only ones in our set of modular sublattices without full $m\bar{3}m$ symmetry, two modular lattices L_0 that differ only in which of the two T lattices they have as a sublattice, are related by a 90 degree rotation and therefore belong to the same Bravais class. We must therefore keep in mind both forms of T lattice only when both are present as sublattices of L_0.

We now enumerate the Bravais classes of the modular lattices (and hence the general rank-6 cubic Bravais classes) according to which of the I^*, T, or F^* lattices they contain as sublattices.

1. If L_0 contains only 000, then the full lattice L is just the sum of two incommensurate rank-3 P lattices (each consisting of points with all even coordinates). We call this decomposable Bravais class $P+P$. Note that one also gets $P+P$ (each consisting of points with all integral coordinates) when L_0 contains all $2^6 = 64$ possible points, as well as when L_0 contains all $2^3 = 8$ possible multiples of k only, k' only (or, as a consequence of reindexing, $k+k'$ only). These cases, examples of point (v) in our initial summary of the method, will emerge later on in our systematic enumeration.

2. If L_0 contains only a single one of the I^* sublattices given in (2.24) (as noted above it does not then matter which) then L is just the sum of incommensurate rank-3 P and I^* lattices. The order is immaterial and we call the resulting decomposable Bravais class $P + I^*$ or $I^* + P$ (or $P + F$ or $F + P$).

3. If L_0 contains only a single one of the F^* sublattices given in (2.25) (as noted above it does not matter which) then L is just the sum of incommensurate rank-3 P and F^* lattices. The order is immaterial and we call the resulting decomposable Bravais class $P + F^*$ or $F^* + P$ (or $P + I$ or $I + P$).

4. If L_0 contains only a single T sublattice (2.26) (as noted above it does not matter which) then L has only tetrahedral symmetry and is an indecomposable rank-6 cubic lattice, which we call T_{F^*} (F for "face centered", as explained below). The indecomposability of T_{F^*} follows from the fact that if it were the sum of two rank-3 lattices, necessarily with full cubic symmetry, it would have to have full cubic symmetry itself, since all four 3-fold axes would have to coincide to maintain the tetrahedral symmetry.[14]

If a modular lattice L_0 contains both types of T sublattices then it must contain their sum, and by listing the sums of the 16 pairs of vectors from the two types one immediately establishes that L_0 must also contain all three of the F^* sublattices. In the same way, one establishes that if L_0 contains any two of the three F^* sublattices, then it must contain the third and also both T sublattices. Finally, if L_0 contains one T sublattice and one F^* sublattice it again must contain all sublattices of both types.

Thus if L_0 contains any of the T or F^* sublattices, it contains either a single one of them, or all five. There can therefore be only one more Bravais class containing none of the I^* sublattices:

[14]It can, however, be viewed as a sum of two rhombohedral rank-3 lattices, with lattice constants and angles cunningly adjusted to give the larger tetrahedral symmetry group to the sum. This view of the T_{F^*} lattice (and the other two tetrahedral lattices that emerge below) has been exploited to construct a very simple computation of the icosahedral space groups (see Mermin[8]), and is similarly well suited for computing the rank-6 space groups on the three tetrahedral lattices (See Dräger *et al.*[3]).

5. If L_0 is the sum of all five T and F^* sublattices then it is easily verified to be the direct sum of two rank-3 F^* lattices, a Bravais class we call $F^* + F^*$ (or $I + I$).

We next note that if a modular lattice L_0 does contain any of the type I^* sublattices, then it contains either a single one or all three. Case 2 above took L_0 to consist of a single I^* sublattice, so there is at most one additional Bravais class containing none of the four-element sublattices of type T or F^*:

6. If L_0 is the sum of all three I^* sublattices then it is easily verified to be the direct sum of two rank-3 I^* lattices, a Bravais class we call $I^* + I^*$ (or $F + F$).

We are left with the modular lattices that contain at least one of the I^* and at least one of the T or F^* sublattices. We first consider the result of combining just a single sublattice from each of these two groups. If we keep available all five varieties of the T and F^* sublattices, then reindexing permits us to consider only a single specimen of the I^* sublattices, which we can take to be $\{k(111)\}$. As noted above, it also suffices to consider a single one of the two T sublattices, and we therefore have just four cases to examine. Combining $\{k(111)\}$ with the F^* sublattice $\{k(110)\}$ gives us just the rank-6 $P + P$ lattice again (this time in a version in which the k sublattice has all integral coordinates and the k' sublattice, only even coordinates). Combining $\{k(111)\}$ with the F^* sublattice $\{(k + k')(110)\}$ gives us back rank-6 $P + F^*$ (in the version in which P occurs with all integral coordinates). The remaining two possibilities give us something new:

7. Combining $\{k(111)\}$ with the F^* sublattice $\{k'(110)\}$ gives us the direct sum of rank-3 I^* and F^* lattices, a Bravais class we call $I^* + F^*$ or $F^* + I^*$ (or $F + I$ or $I + F$).

8. Combining $\{k(111)\}$ with the T sublattice $\{(k, k', k + k')\}$ gives us a second indecomposable lattice with tetrahedral symmetry, which we call T_P (P for "primitive", as explained below). The lattice T_P cannot be equivalent to T_{F^*} since their modular lattices have 8 and 4 elements, respectively. (Equivalences as in step (v) above can only change the number of vectors in a cubic modular lattice by factors of 8.)

There remain only modular lattices that contain either all three of the I^* sublattices (*i.e.* that contain $I^* + I^*$) or all five of the T or F^* sublattices (*i.e.* that contain $F^* + F^*$). (If all three I^* *and* all five T or F^* lattices are present, then L_0 contains all 64 points and we have $P + P$ again.) Since either of these large sublattices is invariant under the reindexing transformations (2.17), it is sufficient to consider combining $F^* + F^*$ with just a single specimen of the I^* sublattice, and $I^* + I^*$ with just a single specimen of the F^* or T sublattices. But combining $F^* + F^*$ with the I^* sublattice $\{k(111)\}$ just gives another version of $P + F^*$, and combining $I^* + I^*$ with the F^* sublattice $\{k(110))\}$ just gives $P + I^*$, so there is only one additional case:

9. Combining $\{I^* + I^*\}$ with the T sublattice $\{(k, k', k + k')\}$ gives us a third indecomposable tetrahedral lattice which we call T_{I^*}. Its modular lattice has 16 elements, and is therefore not equivalent to either of the other two.

Our nomenclature for the three tetrahedral Bravais classes comes from the nomenclature used by Rokhser, Mermin, and Wright[11] for the corresponding icosahedral Bravais classes one gets by letting the incommensurate ratio k/k' tend to the golden mean $(1 + \sqrt{5})/2$. One can verify that all the lattices can be generated by the six vectors

$$\begin{array}{ccc} (k, k', 0) & (0, k, k') & (k', 0, k) \\ (k, -k', 0) & (0, k, -k') & (-k', 0, k) \end{array} \tag{2.27}$$

with primitive indexing (T_P), with the sum of all indices even (T_{F^*}), or with all indices having the same parity (T_{I^*}).

This completes the enumeration of the 9 rank-6 cubic and tetrahedral Bravais classes. The results of this enumeration are summarized in Table 2.2.

2.3.5 The Tetragonal and Axial Monoclinic Cases

Tetragonal rank-4 lattices must have the unique incommensurate direction along the 4-fold c-axis, since otherwise the 4-fold symmetry would require a lattice of rank greater than 4. Monoclinic lattices, on the other hand, have point group $G = 2/m$, and can therefore have a unique direction either along or perpendicular to the 2-fold c-axis. Monoclinic rank-4 lattices with the unique direction along $\mathbf{c}$ (axial monoclinic) and all tetragonal rank-4 lattices can be classified by essentially the same analysis we used in the orthorhombic case, once one notes the following:

As in the orthorhombic and cubic cases, twice the projection of any vector of L along the c-axis is itself in L. Therefore, as argued in section 2.3.2 above, the set of projections of all vectors along that axis can be expressed as a set of linear combinations of two vectors $k\mathbf{c}$ and $k'\mathbf{c}$ with an even sublattice that is primitively indexed. Furthermore since all lattices have inversion symmetry, the plane perpendicular to the c-axis is a mirror plane, and therefore L contains twice the projection of any of its vectors in that plane. Since $2P_\perp L$ is itself a two dimensional lattice (with 4-fold symmetry in the tetragonal case, and only the minimum 2-fold symmetry in the monoclinic case), it can always be primitively indexed in terms of two vectors $\mathbf{a}$ and $\mathbf{b}$ (which are orthonormal in the tetragonal case and arbitrary in the monoclinic case). We can again scale those lattices so that $P_\perp L$ can be indexed by integral linear combinations of $\mathbf{a}$ and $\mathbf{b}$ in such a way that the even sublattice is primitively indexed. We are thus back to a study of the modular lattices L_0 with integral coordinates taken modulo 2.

The analysis of the modular sublattices in the monoclinic case is identical to our analysis of the orthorhombic case in section 2.3.3. We conclude that aside from the two trivial lattices — sums of either the monoclinic P (to which orthorhombic P or C degenerate) or monoclinic C–lattices (to which orthorhombic I^* or F^* degenerate)

with incommensurate 1-dimensional lattices along **c**— there is a third non-trivial lattice (decomposable into a sum of two rank-2 lattices) whose modular lattice L_0 is given by (2.10). We call the trivial lattices $P+1_c$ and $C+1_c$, and the non-trivial lattice, M. The subscript c is to distinguish these from the trivial planar monoclinic lattices $P+1_{ab}$ and $C+1_{ab}$.

In the tetragonal case the analysis is again identical to that for the orthorhombic case, except that we must additionally impose 4-fold symmetry in the plane perpendicular to **c**, which restricts us to modular lattices that contain $n_2n_1n_3n_3'$ whenever they contain $n_1n_2n_3n_3'$. The non-trivial lattice (2.8) does not satisfy this condition, and is therefore excluded. The only tetragonal rank-4 lattices are thus the two trivial extensions of the rank-3 P and C lattices, which we call $P+1$ and $C+1$.

2.3.6 The Trigonal and Hexagonal Cases

We can discuss together the trigonal and hexagonal rank-4 Bravais classes as ones containing lattices L with point groups having a 3-fold axis which may or may not also be 6-fold, taken to be along **c**. If $D = 4$ it must be that the unique incommensurate direction is along the 3-fold axis. The 3-fold symmetry also requires L to contain *three* times the projection of any of its vectors along the 3-fold axis. Consequently the rank-2 lattice L^c of projections of vectors in L along the c-axis can be expressed as integral linear combinations $nk\mathbf{c}+n'k'\mathbf{c}$ with primitive indexing for the subset of points having both n and n' multiples of *three*. Thus the two components along **c** of vectors in the modular lattice L_0 can be taken from the integers modulo 3, which we represent by the three numbers 1, 0, and $\bar{1} = -1$.

The horizontal components of vectors in the modular lattice L_0 are treated exactly as in the periodic case. One first notes that the sublattice L^{ab} of L in the ab plane is a triangular lattice generated primitively by two vectors **a** and $R\mathbf{a}$= **b**, with R a 120° rotation. We can therefore take the lattice L_P with respect to which the modular lattice L_0 is defined, to be the hexagonal $P+1$ lattice generated primitively by **a**, **b**, $3k\mathbf{c}$, and $3k'\mathbf{c}$. If **k** is any vector of L, then $(1-R)\mathbf{k}$ is in the ab–plane. It follows that the projection $P_{ab}\mathbf{k}$ of any vector **k** of L in the ab plane is either itself in L^{ab}, or becomes a vector of $L^{ab}$when acted upon by $(1-R)$. As a result if $P_{ab}\mathbf{k}$ is not in L^{ab} then it can be taken, up to an additive vector of L^{ab}, to be either **d** or $-\mathbf{d}$=$\bar{\mathbf{d}}$, where $\mathbf{d} = \frac{1}{3}(2\mathbf{a}+\mathbf{b})$. Consequently L_0^{ab}, the sublattice of the modular lattice L_0 in the ab–plane is either the single vector 0, or the three vectors **d**, 0, and $-\mathbf{d}$.

If L_0^{ab} contains all three vectors, then the Bravais class is just a trivial sum of a rank-3 hexagonal P lattice (with three times the density of vectors in the ab plane as the hexagonal rank-3 sublattice L_P) with an incommensurate rank-1 lattice along c. Non-trivial rank-4 lattices can thus arise only if L_0^{ab} contains the 0 vector alone. In that case for each of the nine choices for n_3n_3' there can be at most one vector in

the modular lattice L_0 of the form $n_1 n_2 n_3 n_3'$. The only possibilities for a non-zero modular lattice are therefore either a set of three vectors of the form

$$[0000 \quad \mathbf{u}\, n_3 n_3' \quad -\mathbf{u}\, \bar{n}_3 \bar{n}_3'], \tag{2.28}$$

or the set of all nine integral linear combinations modulo 3 of two vectors of the form

$$\mathbf{v}\, 01 \quad \text{and} \quad \mathbf{w}\, 10, \tag{2.29}$$

where $\mathbf{v}$ and $\mathbf{w}$ can each be one of the three vectors $\mathbf{d}$, 0, or $-\mathbf{d}$.

In the former case, the lattice is again trivial, since a reindexing transformation can always be found to make all fourth components zero, so a non–trivial modular lattice must contain vectors of both forms (2.29) along with all their modulo–3 linear combinations. If either $\mathbf{v}$ or $\mathbf{w}$ is zero then L_0 is once again trivial,[15] so there are only two distinct candidates for a non–trivial modular lattice:

$$L_0 = \{\mathbf{d}\, 10 \quad \mathbf{d}\, 01\} \quad \text{or} \quad L_0 = \{\mathbf{d}\, 10 \quad \bar{\mathbf{d}}\, 01\}, \tag{2.30}$$

where here the curly brackets indicate the lattice generated by all modulo–3 integral linear combinations of the vectors within them. The first of these can be written as the sum

$$L_0 = [0000 \quad \mathbf{d}\, 10 \quad \bar{\mathbf{d}}\, \bar{1}0] + [0000 \quad 00\bar{1}1 \quad 001\bar{1}], \tag{2.31}$$

while the second is

$$L_0 = [0000 \quad \mathbf{d}\, 10 \quad \bar{\mathbf{d}}\, \bar{1}0] + [0000 \quad 0011 \quad 00\bar{1}\bar{1}]. \tag{2.32}$$

But by reindexing we can alter (2.31) (or (2.32)) by the result of adding each 4th component (or the negative of each 4th component) to each 3rd component. In either case this gives

$$L_0 = [0000 \quad \mathbf{d}\, 10 \quad \bar{\mathbf{d}}\, \bar{1}0] + [0000 \quad 0001 \quad 000\bar{1}], \tag{2.33}$$

which is just the trivial sum of a $rank - 3$ rhombohedral R lattice with an incommensurate rank-1 lattice along $\mathbf{c}$(consisting of all integral multiples of $k'\mathbf{c}$).

Consequently the only two hexagonal and trigonal rank-4 Bravais classes are the trivial $P + 1$ and $R + 1$ classes. We shall enumerate these Bravais classes again in the following chapters using a different method which uses the fact that they are reducible into a horizontal triangular sublattice and additional rank-1 lattices with non-zero components along the c direction just as are the rank-3 hexagonal and trigonal lattices.

[15] It is explicitly trivial when $\mathbf{v}$=0, and seen to be trivial after a reindexing transformation that interchanges the third and fourth components when $\mathbf{w}$=0.

2.3.7 The Triclinic and Planar Monoclinic Cases

The symmetry of lattices in these Bravais classes is so low that they are better analyzed directly, without using the modular lattice method. We enumerate them here for the sake of completeness.

Lattices L in the triclinic rank-4 Bravais class are generated by 4 integrally independent non-coplanar vectors bearing no special relations to one another, so that the point group G of L contains only the inversion. Since any rank-4 lattice (in any Bravais class) can be generated primitively by four vectors, and since all rank-4 lattices have at least the triclinic point group G, it follows from the definition of Bravais class equivalence in section 2.2.2, that all triclinic rank-4 lattices are in the same Bravais class.

The planar monoclinic Bravais class contains lattices generated by 3 integrally independent vectors in the ab plane and a 4th vector not in the plane of the first 3. Their point group G contains a 2-fold axis $\mathbf{c}$ perpendicular to the ab plane. Because there are no special relations between the generating vectors in the ab plane, the 2-dimensional sublattice L^{ab} can be primitively generated by three vectors $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{d}$. The full rank-4 lattice, as in the rank-3 case, is given by the sum of L^{ab} and the rank-1 lattice consisting of integral multiples of a vector $\mathbf{c} + \mathbf{s}$, where the vector $\mathbf{s}$ is in the ab plane and only determined to within an additive vector of L^{ab}. Two-fold symmetry about the axis $\mathbf{c}$ requires $2\mathbf{s}$ to be in the 2-dimensional rank-3 sublattice L^{ab}. If $2\mathbf{s} = 0$, then the resulting structure can be viewed as a $P + 1_{ab}$ lattice — the sum of a rank-3 monoclinic P lattice with all integral multiples of an integrally independent vector in the ab plane. If $2\mathbf{s}$ is non-zero then $\mathbf{s}$ must be a linear combination of $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{d}$, with coefficients which can be taken to be either 0 or $\frac{1}{2}$, so that $2\mathbf{s}$ is an integral linear combination with coefficients that are either 0 or 1. As a result, we can find a new set of three primitive generating vectors for L^{ab} one of which is $2\mathbf{s}$ itself. The lattice L therefore contains a rank-3 centered monoclinic sublattice consisting of the sum of a rank-2 centered rectangular lattice in the plane of $\mathbf{c}$ and $\mathbf{s}$, added to a rank-1 lattice in a general direction in the ab plane. The full rank-4 lattice L is the sum of this centered monoclinic B lattice and a second rank-1 lattice in the ab plane. We denote the Bravais class by $B + 1_{ab}$. These two trivial lattices are the only rank-4 monoclinic lattices with the incommensurate direction lying in the ab plane.

This completes the enumeration of all sixteen 3-dimensional rank-4 Bravais classes and of the nine rank-6 cubic and tetrahedral Bravais classes. They are listed in Tables 2.1 and 2.2, along with their settings for describing incommensurately modulated crystals, equivalent to 38 corresponding JJdW Bravais classes, as we now show.

Table 2.1: The 3-dimensional rank-4 Bravais classes. The settings for describing incommensurately modulated crystals are given in the second and third columns by their JJdW symbols and numbers. All the Bravais classes are trivial (3+1 decomposable) except for the monoclinic M and orthorhombic O classes, which are decomposable into a sum of two rank-2 centered rectangular lattices.

Triclinic				
$P+1$	$P(\alpha\beta\gamma)$	*1*		
Monoclinic				
$P+1_{ab}$	$P2/m(\alpha\beta0)$	*2*		
$B+1_{ab}$	$B2/m(\alpha\beta0)$	*4*	$P2/m(\alpha\beta\frac{1}{2})$	*3*
$P+1_c$	$P2/m(00\gamma)$	*5*		
$C+1_c$	$B2/m(00\gamma)$	*7*	$P2/m(\frac{1}{2}0\gamma)$	*6*
M	$B2/m(0\frac{1}{2}\gamma)$	*8*		
Orthorhombic				
$P+1$	$Pmmm(00\gamma)$	*9*		
I^*+1	$Fmmm(00\gamma)$	*17*	$Pmmm(\frac{1}{2}\frac{1}{2}\gamma)$	*11*
F^*+1	$Immm(00\gamma)$	*12*	$Cmmm(10\gamma)$	*14*
$C+1$	$Cmmm(00\gamma)$	*13*		
$A+1$	$Ammm(00\gamma)$	*15*	$Pmmm(0\frac{1}{2}\gamma)$	*10*
O	$Ammm(\frac{1}{2}0\gamma)$	*16*	$Fmmm(10\gamma)$	*18*
Tetragonal				
$P+1$	$P4/mmm(00\gamma)$	*19*		
$I+1$	$I4/mmm(00\gamma)$	*21*	$P4/mmm(\frac{1}{2}\frac{1}{2}\gamma)$	*20*
Trigonal				
$R+1$	$R\bar{3}m(00\gamma)$	*22*	$P\bar{3}1m(\frac{1}{3}\frac{1}{3}\gamma)$	*23*
Hexagonal				
$P+1$	$P6/mmm(00\gamma)$	*24*		

Table 2.2: The 3-dimensional rank-6 cubic and tetrahedral Bravais classes. All Bravais classes with full cubic symmetry are decomposable into two rank-3 cubic Bravais classes. The three tetrahedral Bravais classes are not. The 3+3 settings are listed to the right of each Bravais class, given by their JJdW symbol and the numbers assigned to them in Ref. [5]. The indecomposable Bravais class T_{F^*} is represented by the four vector modular lattice $L_0 = [000,000 \;\; 110,011 \;\; 011,101 \;\; 101,110]$, the class T_P by the (eight vector) sum $L_0 + [000,000 \;\; 111,000]$, and the class T_{I^*} by the (sixteen vector) sum $L_0 + [000,000 \;\; 111,000 \;\; 000,111 \;\; 111,111]$. The tetrahedral lattices can be generated by the six vectors $(1, \pm\alpha, 0)$, $(0, 1, \pm\alpha)$, and $(\pm\alpha, 0, 1)$ with primitive indexing (T_P), with the sum of all indices even (T_{F^*}), or with all indices having the same parity (T_{I^*}). When α is equal to the golden mean $(1+\sqrt{5})/2$ these become the three types of icosahedral lattices.

Cubic			
$P + P$	$Pm3m(\alpha 00)$ *208*		
$I^* + I^*$	$Fm3m(\alpha\alpha\alpha)$ *217*		
$F^* + F^*$	$Im3m(0\beta\beta)$ *213*		
$P + I^* = I^* + P$	$Pm3m(\alpha\alpha\alpha)$ *215*	$Fm3m(\alpha 00)$ *211*	
$P + F^* = F^* + P$	$Pm3m(0\beta\beta)$ *212*	$Im3m(\alpha 00)$ *210*	
$I^* + F^* = F^* + I^*$	$Im3m(\alpha\alpha\alpha)$ *216*	$Fm3m(\alpha 00)$ *214*	$Pm3m((\alpha\frac{1}{2}\frac{1}{2})$ *209*
Tetrahedral			
T_P	$Fm3(1\beta\beta+1)$ *207*	$Pm3(\alpha\frac{1}{2}0)$ *204*	
T_{F^*}	$Pm3(\frac{1}{2}\beta\beta+\frac{1}{2})$ *206*		
T_{I^*}	$Fm3(\alpha 10)$ *205*		

2.4 Computation of the Lattices of Main Reflections

For each rank-4 Bravais class (and rank-6 cubic or tetrahedral Bravais class) it is useful to examine of its distinct (3+1) (or (3+3)) reducible forms, giving its settings for the description of incommensurately modulated crystals and composite crystals. In all cases considered here the lattices are simple enough that the settings, which identify the invariant rank-3 sublattice of main reflections, are characterized by the rank-3 Bravais class to which the sublattice belongs. There are never distinct settings in which the sublattices of main reflections belong to the same Bravais class. We shall see in Chapter 4 that in general this is not always the case.

We will continue to use the modular lattice description for extracting the rank-3 Bravais classes that can be associated in this way with a given rank-D Bravais class. The procedure is simplest if one choses the modular lattice with the smallest number of vectors, whenever a rank-D Bravais class can be described by several distinct modular lattices (as in point (v) section 2.3.1).

Each of our settings corresponds exactly to one of the JJdW Bravais classes for incommensurately modulated crystals. We emphasize this correspondence by denoting the settings with the corresponding JJdW Bravais-class symbol, both in text that follows, and in Tables 2.1 and 2.2 which summarize the results obtained here.

2.4.1 Lattices of Main Reflections in the Orthorhombic, Tetragonal, and Axial Monoclinic Cases.

Orthorhombic case.

We show below that two of the six orthorhombic Bravais classes ($P+1$ and $C+1$) contain rank-4 lattices with rank-3 sublattices lattices from a unique rank-3 Bravais class. The non-trivial Bravais class O, however, and the three trivial classes I^*+1, F^*+1, and $A+1$, contain rank-4 lattices that have rank-3 sublattices from two distinct rank-3 Bravais classes, giving two settings for each of these classes, and a total of 10 JJdW Bravais classes.

a. A lattice in the I^*+1 ($F+1$) Bravais class can be described by the modular lattice

$$[0000 \;\; 1110], \tag{2.34}$$

which represents it as the trivial extension of a rank-3 I^* lattice and an incommensurate rank-1 lattice along $\mathbf{c}$ (with lattice constant $2k'$). Because all vectors in the rank-1 lattice are 0 modulo the even sublattice L_P, the rank-1 lattice does not appear explicitly in (2.34). To emphasize its presence one could rewrite (2.34) as $[0000 \;\; 1110] + [0000]$. A similar remark applies to the other trivial Bravais classes, and also to Bravais classes containing rank-3 P sublattices, when they contain only the 0 vector modulo L_P. A reindexing transformation that interchanges the third

and fourth components does not change the Bravais class, but converts (2.34) into

$$[0000 \;\; 1101]. \tag{2.35}$$

This now represents the lattice as the sum of a rank-3 P lattice (given by the lattice L_P, whose presence may be emphasized by rewriting (2.35) as [0000]+[0000 1101]) and the rank-1 lattice consisting of arbitrary integral multiples of $\mathbf{a}+\mathbf{b}+k'\mathbf{c}$. None of the other reindexing transformations (2.3) give rank-3 sublattices in any other rank-3 Bravais classes. These two forms of the I^*+1 Bravais class appear as two distinct Bravais classes in the catalog of JJdW: the first, as $Fmmm(00\gamma)$ and second as $Pmmm(\frac{1}{2}\frac{1}{2}\gamma)$.

b. A lattice in the F^*+1 ($I+1$) Bravais class can be described by the modular lattice

$$[0000 \;\; 1100 \;\; 1010 \;\; 0110], \tag{2.36}$$

which represents it as the trivial extension of a rank-3 F^* lattice by a 1-dimensional lattice along $\mathbf{c}$ (with lattice constant $2k'$). Interchanging the 3rd and 4th components (a reindexing transformation that does not alter the Bravais class) changes this to

$$[0000 \;\; 1100 \;\; 1001 \;\; 0101], \tag{2.37}$$

which we can express as the sum of two smaller modular lattices:

$$[0000 \;\; 1100] + [0000 \;\; 1001]. \tag{2.38}$$

In this form the first modular lattice describes a sublattice in the rank-3 C Bravais class, and the second adds to it the rank-1 lattice of integral multiples of $\mathbf{a}+k'\mathbf{c}$. None of the other reindexing transformations lead to any other rank-3 sublattices, so we arrive at two ways of viewing the F^*+1 Bravais class: the first occurs in the JJdW catalogue as $Immm(00\gamma)$ and the second, as $Cmmm(10\gamma)$.

c. A lattice in the $A+1$ Bravais class can be described by the modular lattice

$$[0000 \;\; 0110]. \tag{2.39}$$

The reindexing transformation, interchanging the 3rd and 4th components, changes this to

$$[0000 \;\; 0101], \tag{2.40}$$

which describes the sum of a rank-3 P lattice (given by the even sublattice L_P) with the rank-1 lattice of integral multiples of $\mathbf{b}+k'\mathbf{c}$. None of the other reindexing transformations lead to any other rank-3 sublattices and we have two alternative descriptions of the $A+1$ Bravais class, which occur in JJdW as $Ammm(00\gamma)$ and $Pmmm(0\frac{1}{2}\gamma)$.

d. The single non-trivial orthorhombic Bravais class, O has the modular lattice given by (2.8):

$$[0000 \;\; 1010 \;\; 0101 \;\; 1111]. \tag{2.41}$$

which can also be written as

$$[0000\ \ 1010] + [0000\ \ 0101]. \tag{2.42}$$

In this form it is written as the direct sum of two 2-dimensional centered rectagonal lattices, one in the ac plane and the other in the bc plane. It can also be viewed as the sum of a rank-3 B-centered orthorhombic lattice with a rank-1 lattice of integral multiples of $\mathbf{b} + k'\mathbf{c}$. If, however, we apply to (2.41) the reindexing transformation that adds the 3rd component to the 4th, we get

$$[0000\ \ 1011\ \ 0101\ \ 1110], \tag{2.43}$$

which can be written as

$$[0000\ \ 1110] + [0000\ \ 0101]. \tag{2.44}$$

This displays it as a the sum of a rank-3 I^* (F) lattice and a rank-1 lattice of integral multiples of $\mathbf{b} + k'\mathbf{c}$. The other reindexing transformations give no other rank-3 sublattices (though they can transform the B setting to the A setting) and we have the JJdW Bravais classes $Ammm(\frac{1}{2}0\gamma)$ and $Fmmm(10\gamma)$.

The $P + 1$ Bravais class can be represented by the modular lattice containing only 0, which clearly generates no other rank-3 sublattices under reindexing, and the $C + 1$ Bravais class can be represented by [0000 1100] which is also invariant under reindexing. These two therefore admit rank-3 sublattices from only a single rank-3 Bravais class, and correspond to unique Bravais classes of JJdW: $Pmmm(00\gamma)$ and $Cmmm(00\gamma)$.

Tetragonal case.

These results are immediately carried over to the tetragonal case, where the orthorhombic $P + 1$ and $C + 1$ rank-4 Bravais classes become identified, as do $I^* + 1$ and $F^* + 1$. (The orthorhombic $A + 1$ and O Bravais classes do not exist in the tetragonal system.)

The tetragonal $P + 1$ Bravais class has therefore a unique representation which is JJdW's $P4/mmm(00\gamma)$. The centered tetragonal $I^* + 1$ Bravais class, however, inherits from its orthorhombic parent a pair of representations: $I4/mmm(00\gamma)$ or $P4/mmm(\frac{1}{2}\frac{1}{2}\gamma)$.

Axial monoclinic case.

In the monoclinic case, the $P + 1_c$ Bravais class again contains a unique class of rank-3 sublattices, and therefore can be described only as JJdW's $P2/m(00\gamma)$. The $B + 1_c$ Bravais class, however, has the modular lattice

$$[0000\ \ 1010] \tag{2.45}$$

which displays a rank-3 centered monoclinic sublattice. Interchanging the 3rd and 4th components gives

$$[0000 \quad 1001], \tag{2.46}$$

which now describes the sum of a monoclinic rank-3 P lattice, and the rank-1 lattice of integral multiples of $\mathbf{a}+k'\mathbf{c}$. These thus the $B+1_c$ Bravais class appears in JJdW both as $B2/m(00\gamma)$ and as $P2/m(\frac{1}{2}0\gamma)$.

The non-trivial monoclinic M lattice has the modular lattice

$$[0000 \quad 0101 \quad 1010 \quad 1111], \tag{2.47}$$

which can be written as

$$[0000 \quad 1010] + [0000 \quad 0101]. \tag{2.48}$$

This describes the sum of a rank-3 B lattice with the rank-1 lattice of integral multiples of $\mathbf{b}+k'\mathbf{c}$, which appears in the JJdW catalog as $B2/m(0\frac{1}{2}\gamma)$. Various reindexing transformations only reveal other centered monoclinic rank-3 sublattices.

2.4.2 Lattices of Main Reflections in the Trigonal and Hexagonal Cases

Since the $P+1$ Bravais class can be represented with a modular lattice consisting of 0 alone, it has no rank-3 sublattice other than the P lattice and occurs only as $P6/mmm(00\gamma)$ of JJdW. The $R+1$ Bravais class, however, can be described most simply in terms of the modular lattice:

$$[0000 \quad \mathbf{d}\,10 \quad \bar{\mathbf{d}}\,\bar{1}0], \tag{2.49}$$

which describes the sum of a rank-3 R lattice and the rank-1 lattice of integral multiples of $3k'\mathbf{c}$. This is JJdW's $R\bar{3}m(00\gamma)$. Interchanging the 3rd and 4th components gives

$$[0000 \quad \mathbf{d}\,01 \quad \bar{\mathbf{d}}\,0\bar{1}], \tag{2.50}$$

which now describes the sum of a rank-3 P lattice and the rank-1 lattice of integral multiples of $k'\mathbf{c}+\mathbf{d}$, which is JJdW's $P\bar{3}1m(\frac{1}{3}\frac{1}{3}\gamma)$.

2.4.3 Lattices of Main Reflections in the Planar Monoclinic Case

Lattices in the monoclinic $P+1_{ab}$ Bravais class have no rank-3 sublattices other than the P lattice, and the class appears in JJdW only as $P2/m(\alpha\beta 0)$. The $B+1_{ab}$ Bravais class, however, can be represented with the modular lattice

$$[0000 \quad 1010], \tag{2.51}$$

where we have taken the 3rd position to describe the c-axis, and have associated the 1st, 2nd, and 4th positions with the 3 integrally independent vectors **a**, **b**, and **d** in the ab plane, so that (2.51) describes the trivial sum of a centered monoclinic B-lattice and the rank-1 lattice (not shown explicitly) consisting of even multiples of **d** ($= \alpha\mathbf{a} + \beta\mathbf{b}$) given by JJdW as $B2/m(\alpha\beta 0)$. If we reindex in the ab plane by interchanging the first and 4th components we change (2.51) to

$$[0000 \;\; 0011], \tag{2.52}$$

which describes the sum of a rank-3 P lattice (not shown explicitly) and the rank-1 lattice of integral multiples of $\mathbf{c} + \mathbf{d}$, which is JJdW's $P2/m(\alpha\beta\frac{1}{2})$.

2.4.4 Lattices of Main Reflections in the Cubic Case

As with the rank-4-lattices, the question of what sublattices of main reflections can be associated with the 9 cubic rank-6 Bravais classes is simply the question of what rank-3 sublattices of the form

$$n_1 n_2 n_3, \;\; 000 \tag{2.53}$$

are contained in the rank-6 lattices in the class. There is one point which is less obvious here than in the rank-4 case and is worth emphasizing. Expressing a lattice in one of its settings is equivalent to finding a basis of which the first three vectors generate the sublattice of main reflections. One should not forget that the full set of six vectors is indeed a basis and must generate the full rank-6 lattice. Thus one can always find a modular lattice of the form (2.53) which contains only the zero vector. This does not imply that every rank-6 cubic lattice contains a rank-3 P lattice of main reflections. This is only the case if all other vectors in the modular lattice of the full rank-6 lattice can be generated by no more than three additional generators, giving a total of six generators.

Clearly, lattices in the six decomposable Bravais classes contain sublattices of main reflections in their constituent rank-3 Bravais classes. This gives two settings in each of the following Bravais classes: $P + F^*$, given by JJdW as $Pm3m(0\beta\beta)$ and $Im3m(\alpha 00)$; $P + I^*$, given by JJdW as $Pm3m(\alpha\alpha\alpha)$ and $Fm3m(\alpha 00)$; and $F^* + I^*$, given by JJdW as $Im3m(\alpha\alpha\alpha)$ and $Fm3m(0\beta\beta)$; and gives a single setting in each of the following Bravais classes: $P + P$, given as $Pm3m(\alpha 00)$; $I^* + I^*$, given as $Fm3m(\alpha\alpha\alpha)$; and $F^* + F^*$, given as $Im3m(0\beta\beta)$.

One verifies easily that the only decomposable Bravais class whose lattices contain an additional setting, beyond the obvious ones just mentioned, is the $F^* + I^*$ Bravais classes whose lattices contain also rank-3 P sublattices of main reflections. To see this note that $F^* + I^*$ is characterized by the 8-element modular lattice:

$$\begin{array}{l} [000,000 \;\; 110,000 \;\; 101,000 \;\; 011,000] + [000,000 \;\; 000,111] = \\ [000,000 \;\; 110,000 \;\; 101,000 \;\; 011,000 \\ \;\; 000,111 \;\; 110,111 \;\; 101,111 \;\; 011,111]. \end{array} \tag{2.54}$$

This is in the same rank-6 Bravais class as the form it assumes under the reindexing transformation $\mathbf{n}, \mathbf{n}' \rightarrow \mathbf{n}, \mathbf{n}+\mathbf{n}'$:

$$\begin{array}{llll}[000,000 & 110,110 & 101,101 & 011,011 \\ 000,111 & 110,001 & 101,010 & 011,100].\end{array} \tag{2.55}$$

This has a rank-3 sublattice consisting of the 0 vector alone. It describes the sum of the primitive even sublattice L_P (represented implicitly by [000,000]) and another sublattice given by all integral linear combinations of the three vectors[16]

$$011,100 \quad 101,010 \quad 110,001, \tag{2.56}$$

since these are easily verified to form a basis (modulo-2) for the full set of 8 modulo-2 vectors (2.55). This setting corresponds to JJdW's $Pm3m(\alpha\frac{1}{2}\frac{1}{2})$.

Thus the six decomposable rank-6 cubic Bravais classes with $m\bar{3}m$ symmetry have ten settings altogether, corresponding to the ten Bravais classes of JJdW. The three indecomposable Bravais classes with $m\bar{3}$ symmetry have four settings altogether:

The lattices in the Bravais class T_{F^*} have the four element modular lattice (2.26):

$$[000,000 \quad 110,011 \quad 011,101 \quad 101,110]. \tag{2.57}$$

The reindexing transformations (2.17) simply permute the vectors in this set or rotate them through 90 degrees. None of them alter the fact that the only lattice of main reflections that can be found in the lattices of this Bravais class is the rank-3 P lattice, and therefore the rank-6 lattice (2.57) can be uniquely characterized as a P lattice of main reflections with satellites at the points generated by all integral linear combinations of the 3 non-zero vectors in (2.57).[17] JJdW give this as $Pm3(\frac{1}{2}\beta\beta+\frac{1}{2})$.

Lattices in the Bravais class T_P have eight element modular lattices given by adding to (2.57) one of the I^* lattices (2.24). The various forms allowed by reindexing correspond to the three possible representations for the I^* lattice:

$$\begin{array}{ll}[000,000 & 111,000]; \\ [000,000 & 000,111]; \\ [000,000 & 111,111].\end{array} \tag{2.58}$$

The first form represents T_P as an I^* lattice of main reflections, with satellites at the points about the main reflections generated by all linear combinations of the 3 non-zero vectors in (2.57). This is JJdW's $Fm3(1\beta\beta+1)$. The second and third forms of the I^* lattice yield modular lattices in which only the zero vector has a vanishing component along k', so the lattices of main reflections are the rank-3 P lattice

[16] In the notation of section 2.3.4 we would describe this second sublattice simply as $\{110,001\}$.

[17] In the notation of section 2.3.4 we would describe the modular lattice characterizing the satellites as $\{110,011\}$.

L_P, and the entire set of eight modulo-2 vectors describe the shifts. Depending on whether we use the second or third form of I^* these can be represented as all integral linear combinations of either $101, 100$ or $010, 100$ and their cyclic permutations.[18] The second alternative appears on JJdW's list as $Pm3(\alpha\frac{1}{2}0)$.

The Bravais class T_{I^*} has a 16 element modular lattice given by adding to T_0 the modular lattice $I^* + I^*$:

$$[000, 000, \quad 000, 111 \quad 111, 000 \quad 111, 111]. \tag{2.59}$$

Since this structure is invariant under any of the reindexing transformations and since T_{F^*} is either invariant or rotated by the transformations, T_{I^*} can only have a single representation in terms of a sublattice of main reflections, and this representation is immediately extracted by viewing T_{I^*} as the sum of an I^* rank-3 lattice of main reflections with the satellites described by a T_P rank-6 lattice in the form we identified above as JJdW's $Pm3(\alpha\frac{1}{2}0)$. This corresponds to JJdW's $Fm3(\alpha 10)$.

The rank-3 sublattices of main reflections contained in the lattices of each of the 25 Bravais classes, enumerated in this chapter, are summarized in Table 2.1 (rank-4 lattices) and Table 2.2 (rank-6 cubic and tetrahedral lattices), which specify them by listing which of the 38 JJdW Bravais classes they correspond to.

[18] In the notation of section 2.3.4, as $\{101, 100\}$ or $\{010, 100\}$.

Bibliography

[1] A. Bienenstock, and P. P. Ewald, "Symmetry of Fourier space", *Acta Cryst.* **15** (1962) 1253-1261.

[2] J. Dräger, R. Lifshitz and N. D. Mermin. "Tetrahedral Quasicrystals". To appear in the proceedings of the 5th International Conference on Quasicrystals, Avignon, France, May 22-26, 1995.

[3] J. Dräger, R. Lifshitz and N. D. Mermin. To be submitted to *Acta Cryst.* A.

[4] B. Hartley and T. O. Hawkes, "Rings, modules, and linear algebra", (Chapman and Hall, London, 1970).

[5] A. Janner, T. Janssen, and P. M. de Wolff, "Bravais classes for incommensurate crystal phases", *Acta Cryst.* A**39** (1983) 658-666.

[6] T. Janssen, A. Janner, A. Looijenga-Vos, and P. M. de Wolff, "Incommensurate and commensurate modulated structures", *International Tables for Crystallography, Volume C,* Ed. A. J. C. Wilson (Kluwer Academic, Dodrecht, 1992) 797-844.

[7] R. Lifshitz and N. D. Mermin, "The Symmetry of Composite Crystals". To appear in *Aperiodic '94, An International Conference on Aperiodic Crystals,* Ed. G. Chapuis (World Scientific, Singapore 1995).

[8] N. D. Mermin, "The space groups of icosahedral quasicrystals and cubic, orthorhombic, monoclinic, and triclinic crystals", *Revs. Mod. Phys.* **64** (1992) 3–49.

[9] N. D. Mermin and R. Lifshitz. "Bravais Classes for the Simplest Incommensurate Crystal Phases". *Acta Cryst.* A**48** (1992) 515-532.

[10] W. Opechowski, "Crystallographic and metacrystallographic groups", (North-Holland, Amsterdam, 1986).

[11] D. S. Rokhsar, N. D. Mermin, and D. C. Wright, "Rudimentary crystallography: The icosahedral and decagonal reciprocal lattices", *Phys. Rev* B**35** (1987) 5487–5495.

[12] S. van Smaalen, "Superspace-group approach to the modulated structure of the inorganic misfit layer compound $(LaS)_{1.14}NbS_2$", *J.Phys.:Condens. Matter* **3** (1991) 1247–1263.

Chapter 3

Space Groups of Trigonal and Hexagonal Quasiperiodic Crystals of Rank 4

3.1 Introduction

It is our purpose in this chapter to illustrate the simplicity of the Fourier-space enumeration of space groups on decomposable lattices. We shall show, as a pedagogical example, how to construct the hexagonal and trigonal rank-4 space groups through a simple examination of the Fourier space description of the periodic (rank-3) trigonal and hexagonal space groups. We shall then show explicitly how the classification of modulated crystals emerges from the general case when the general categories are described in their distinct settings to emphasize distinct rank-3 sublattices of main reflections. In Chapter 4 we shall extend these results to hexagonal and trigonal crystals of arbitrary finite rank.

We begin, in section 3.2 by giving a slightly more detailed exposition of the Fourier-space approach than the one given in Chapter 1. In section 3.3 we review the necessary information needed for the enumeration of the rank-4 space groups. This includes a summary of the trigonal and hexagonal point groups; an alternative enumeration of the rank-4 hexagonal and trigonal Bravais classes which is simpler than the one, based on the modular lattice method, given in Chapter 2; and a review of the periodic (rank-3) trigonal and hexagonal space groups. In section 3.4 we show how the relevant phases for rank-4 hexagonal or trigonal quasiperiodic crystals can be read off directly from the phases for hexagonal and trigonal periodic crystals. In section 3.5 we extract from those phases the hexagonal and trigonal rank-4 space groups, and show how the conventional categories for modulated crystals, previously derived by JJdW[8,9,6], can be recovered as different settings of those space groups that emphasize different rank-3 sublattices of main reflections. The complete specifications of the hexagonal and trigonal space groups of rank-4, along with their (3+1) settings for modulated crystals, are summarized in Tables 3.5–3.7.

3.2 Constructing Space Groups in Fourier Space

We give here a slightly more detailed exposition of the Fourier-space approach to the classification of space groups than the one given in the introduction, with emphasis on the practical aspects of enumeration. A more detailed exposition may be found in Mermin[3].

3.2.1 Indistinguishability and Gauge Functions

The key to the reformulation of crystallography in a manner that embraces quasiperiodic as well as periodic materials, is to redefine the *point group* of a material as the subset of operations from $O(3)$ that take the density into one that is *indistinguishable* from what it was. Two densities are said to be indistinguishable if they have the same positionally averaged n-point autocorrelation functions for all n—*i.e.* if any substructure on any scale that occurs in one occurs in the other with the same frequency. From a practical point of view any two densities related in this way are literally indistinguishable, since any finite subregion of one is just as likely to be a subregion of the other, and all laboratory specimens do indeed come in finite chunks.

Formally, densities ρ and ρ' are indistinguishable if

$$\frac{1}{V}\int d\mathbf{r}\rho(\mathbf{r}_1-\mathbf{r})\ldots\rho(\mathbf{r}_n-\mathbf{r}) = \frac{1}{V}\int d\mathbf{r}\rho'(\mathbf{r}_1-\mathbf{r})\ldots\rho'(\mathbf{r}_n-\mathbf{r}) \tag{3.1}$$

for all n. If a material is periodic, one can prove that indistinguishability reduces to identity to within a translation. One can then combine point group operations with translations to recover the traditional space groups of periodic materials, containing operations that leave the density *identical* to what it was. But indistinguishable quasiperiodic densities need not be so simply related in real space. In the conventional terminology of quasiperiodic crystals indistinguishable densities are said to differ by a translation and/or a "phason".

The condition (3.1) of indistinguishability acquires a very simple form in Fourier space that applies equally well to periodic or quasiperiodic crystals. One easily shows that an equivalent condition is that the product of the density Fourier coefficients $\rho(\mathbf{k})$ over any set of wave vectors summing to zero, should agree with the corresponding product for ρ'. This in turn leads, as sketched below, to the condition that ρ and ρ' are indistinguishable if and only if their density Fourier coefficients are related by

$$\rho'(\mathbf{k}) = e^{2\pi i\chi(\mathbf{k})}\rho(\mathbf{k}) \ , \tag{3.2}$$

where χ, called a *gauge function*, is linear modulo an integer over the lattice of wave vectors. Linearity on the lattice means that $\chi(\mathbf{k}_1+\mathbf{k}_2) \equiv \chi(\mathbf{k}_1)+\chi(\mathbf{k}_2)$ whenever $\mathbf{k}_1$ and $\mathbf{k}_2$ are in the lattice, where "$\equiv$" indicates equality modulo an integer. Only when the rank of the lattice is 3, can one always extend χ to a function linear on *all* of continuous $\mathbf{k}$-space.

That $\rho(\mathbf{k})$ and $\rho'(\mathbf{k})$ must differ by at most a phase follows from the identity of the 2-point correlation functions; that those phases must be linear on the lattice follows from the identity of the 3-point correlation functions; and this is then enough to guarantee the identity of the n-point correlation functions.[1]

3.2.2 Gauge-Equivalence Classes of Phase Functions

Because the point group is defined to leave the density indistinguishable, we can associate with each point group operation g a gauge function $\Phi_g(\mathbf{k})$, called a *phase function*, which relates $\rho(g\mathbf{k})$ and $\rho(\mathbf{k})$:

$$\rho(g\mathbf{k}) = e^{2\pi i \Phi_g(\mathbf{k})}\rho(\mathbf{k}) \ . \tag{3.3}$$

The space group of a material in the Fourier-space approach is specified by its point group and its phase functions.

Two sets of phase functions, Φ and Φ', that describe indistinguishable densities ρ and ρ', related by a gauge function χ, should clearly be associated with the same space group. It follows from (3.2) and (3.3) that two such sets must be related by

$$\Phi'_g(\mathbf{k}) \equiv \Phi_g(\mathbf{k}) + \chi([g-1]\mathbf{k}) \tag{3.4}$$

for every g in the point group and every $\mathbf{k}$ in the lattice. We call Φ and Φ' *gauge-equivalent phase functions* and equation (3.4) a *gauge transformation*. Note that since $\chi(0) \equiv 0$, if $g\mathbf{k} = \mathbf{k}$ then the value of $\Phi_g(\mathbf{k})$ is gauge-invariant.

The major part of enumerating the space groups for a given point group consists of finding the families of gauge-equivalent phase functions. We can specify the families by picking one representative for each one, selected by an appropriate choice of gauge to have a conveniently simple form. Because of the linearity of the phase functions they need only be given for a set of primitive lattice-generating vectors. Since $\rho([gh]\mathbf{k}) = \rho(g[h\mathbf{k}])$, it follows from (3.3) that the phase function for the product of two point group operations can be constructed out of the phase functions for the individual operations by the rule

$$\Phi_{gh}(\mathbf{k}) \equiv \Phi_g(h\mathbf{k}) + \Phi_h(\mathbf{k}) \ , \tag{3.5}$$

called the *group compatibility condition*.

Thus each family of gauge-equivalent phase functions is entirely specified by a finite set of phases: the values of a representative member of the family, given at a set of primitive lattice-generating vectors, and for a set of operations that generate the point group. We need to use *primitive* lattice-generating vectors because the group compatibility condition (3.5), which is used in determining these phases, is only required to hold at vectors $\mathbf{k}$ that are in the lattice.

[1] For details see Mermin[3].

The point group generating relations impose, through the group compatibility condition (3.5), a set of constraints on these phases that insure they have a unique value for any point-group operation, independent of how that operation is expressed in terms of the generating operations. These constraints are the generalizations to quasiperiodic materials of the Frobenius congruences in the space group description of periodic materials. To determine the gauge-equivalence classes of phase functions we therefore choose a set of primitive generating vectors for the lattice and a set of generators for the point group. We apply the group compatibility condition to the point-group generating relations to produce a set of constraints on the phases associated with those lattice-generating vectors and point group generators. With a judicious choice of gauge we extract from these constraints a unique representative of each of the possible classes of gauge-equivalent phase functions.

3.2.3 Gauge Equivalence on Decomposable Lattices

A great simplification in the enumeration of gauge-equivalence classes arises when the lattice, on which the phase functions are defined, is decomposable. A decomposable lattice (see section 2.2.3) is a direct sum of lower-rank lattices, each independently invariant under the point group. This means that the application of any point group element to a generating vector belonging to one sublattice will give an integral linear combination of generating vectors from that sublattice and no others.

The set of equations that we solve to determine the gauge-equivalence classes — the group compatibility conditions (3.5) for all the point-group generating relations and all the lattice generating vectors, and the choice of gauge (3.4) — can all be decoupled into independent calculations for each sublattice. This is because only the point group operations g couple the different equations for the individual lattice-generating vectors. Thus if one already knows the possible gauge-equivalence classes for lattices of lower-rank it is not even necessary to recompute them for a decomposable lattice of higher rank. One only needs to consider all the different combinations of the gauge-equivalence classes already classified for the lower rank sublattices. We shall use this decomposition principle here and in Chapter 4.

3.2.4 Scale-Equivalence Classes of Phase Functions

The remaining part of the space group classification is merely a matter of simplifying the bookkeeping by grouping together different gauge-equivalence classes, which ought to be identified on other grounds. Although the grounds for this further identification can be stated quite precisely, whether one chooses to make it or not can be a matter of convention. A useful example to keep in mind is the orthorhombic system of periodic crystals, in which space groups that differ only in the roles played by the a–, b–, or c– axes are not distinguished, even though their phase functions

are not gauge-equivalent. Although they are not distinguished as *space groups*, it can be very useful to distinguish them as distinct *settings* of the same space group.

Such further identifications arise when there is an operation s not in the point group of the material that acts linearly on the lattice L of wave vectors, leaving it invariant, in such a way that $G \rightarrow sGs^{-1}$ continues to describe the action of the point group on the lattice so that s is an automorphism of the point group. Materials characterized by phase functions

$$\Phi'_g(\mathbf{k}) = \Phi_{sgs^{-1}}(s\mathbf{k}) \tag{3.6}$$

cannot be sensibly distinguished on grounds of symmetry from those classified by phase functions $\Phi_g(\mathbf{k})$ and therefore Φ' and Φ should be grouped in the same class.

Operations s that *are* in the point group G have precisely this property, but it is a simple exercise to show directly from (3.5) that for such s, Φ' and Φ are already gauge-equivalent. If s is *not* an element of the point group G, then the two sets of phase functions will not in general be gauge-equivalent. In the interests of simplicity it is then usually, but not always, desirable to make a further identification. For example, if the point group is non-centrosymmetric then the inversion is such an operation s. Whether or not one makes the corresponding identification of gauge-equivalence classes corresponds in the periodic case to whether or not one distinguishes between enantiomorphic pairs of space groups, counting 230 or 219 distinct types. In this case the grounds for not making the further distinction are these: if s is a proper rotation one can interpolate between the materials with the two different gauge-equivalence classes without at any step altering either the point group G or (in the quasiperiodic case) the rank of the lattice. But if s is an improper rotation one cannot. We use "interpolate" in the same sense that it was used in the definition of Bravais class in section 2.2.2.

In the periodic case s can be a rotation. The space group $P\frac{2_1}{a}\bar{3}$, for example, is associated with two distinct gauge-equivalence classes. Here G is a tetrahedral point group and the operation s providing the scale-equivalence is a 90 degree rotation.[2] This is the only example in the rank-3 cubic system of a further scale-equivalence between distinct gauge-equivalence classes. In the periodic case s can also be an element of $O(3)$ combined with a rescaling of the primitive lattice-generating vectors. In the orthorhombic system for example, s can be a 90 degree rotation about any of three orthogonal directions combined with an anisotropic rescaling to reproduce the original lattice. This leads us to view as a single space group such distinct gauge-equivalence classes as $Pamm$, $Pmbm$ and $Pmmc$. The orthorhombic system has many such examples. The distinct gauge-equivalence classes making up a single orthorhombic space group are just the different settings of that space group.

In the quasiperiodic case s can be an isotropic rescaling of the entire lattice, as in the case of icosahedral quasicrystals.[3] It can also be an isotropic rescaling

[2] See Mermin[3, Table VIII, page 23] for details.

[3] See Rokshar, Wright, and Mermin[7] or Mermin[3].

of a sublattice, as in the case of axial quasicrystals,[4] or, in the case of the rank-4 quasiperiodic crystals considered below, independent rescalings of certain lattice-generating vectors. Because rescalings are often (though not always) a part of the transformation s, two classes of gauge-equivalent phase functions that are further identified in this manner are said to be *scale-equivalent*.

The classes of phase functions under gauge-equivalence and scale-equivalence correspond precisely to the space groups in the periodic case, and constitute the extension of the space group classification scheme to the general quasiperiodic case.

3.2.5 The Relation between the Convention used for Scale Equivalence and Space-Group Settings for Modulated Crystals

As we shall see below, the changes of bases which were termed *reindexing transformation* in the previous chapter are the only source of scale-equivalence in the rank-4 hexagonal and trigonal cases considered here. The scale-equivalence of the rank-4 gauge-equivalence classes arises in this case from the existence of two primitive generating vectors with incommensurate components along the direction $\hat{\mathbf{z}}$ of the 3- or 6-fold axis. There is then a freedom to choose other integrally independent pairs of vectors with components along $\hat{\mathbf{z}}$ as generators, without in any way altering the way in which the point group acts on the generating vectors. Such a change of basis can also be viewed as the end point of an interpolating family of operations which independently rescale the $z-$components of both vectors, without at any stage altering either the point group or the rank.

The operations s relevant to scale-equivalence are the linear transformations connecting two such pairs of generating vectors. The sole difference, from the practical point of view of enumeration, between the space groups for general rank-4 crystals and their 3+1 settings for modulated crystals, stems from one additional convention in the modulated case: that the lattice of main reflections should remain independently invariant under transformations s used to establish scale-equivalence. The superspace approach imposes this additional convention at the start of its analysis. In the Fourier space approach the determination of gauge-equivalence classes is simple because it is unencumbered by any such constraints associated with scale-equivalence. The further identifications of gauge-equivalence classes on the basis of scale-equivalence (with whatever constraints one wishes to impose on the allowed transformations s) are easily applied to the gauge-equivalence classes *after* those classes have been enumerated.

[4] See Rabson, Mermin, Rokhsar and Wright[6].

Table 3.1: Point groups of the hexagonal and trigonal systems. All point groups are compatible with the hexagonal P or $P+1$ (VV) lattices, giving for each lattice a total of twelve point groups, four of which ($\bar{6}2m$, $\bar{3}m$, $3m$ and 32) can be oriented in two distinct ways on the hexagonal lattice. Only the point groups with 3-fold symmetry are compatible with the trigonal R or $R+1$ (SV) lattices, giving for each lattice a total of five point groups, each with a unique orientation.

Generators	**Hexagonal**	**Trigonal**
$\bar{\boldsymbol{r}}$	$\bar{6}$	$\bar{3}$
$\bar{\boldsymbol{r}}, \boldsymbol{m}$	$\bar{6}2m$	$\bar{3}m$
$\boldsymbol{r}$	6	3
$\boldsymbol{r}$, $\boldsymbol{m}$	$6mm$	$3m$
$\boldsymbol{r}$, $\boldsymbol{d}$	622	32
$\boldsymbol{r}$, $\boldsymbol{h}$	$6/m$	—
$\boldsymbol{r}$, $\boldsymbol{h}$, $\boldsymbol{m}$	$6/mmm$	—

3.3 Background Information

We now summarize all the information necessary for the enumeration of the space groups and their settings. The enumeration itself will follow in sections 3.4 and 3.5. We first list in section 3.3.1 the point groups and their generators in the hexagonal and trigonal systems. We then give in section 3.3.2 an elementary derivation of the hexagonal and trigonal rank-4 Bravais classes which simplifies the more elaborate derivation given in Chapter 2 using the modular lattice method. Finally, since we plan to exploit the decomposability of the rank-4 hexagonal and trigonal lattices for the enumeration of the space groups, we give in section 3.3.3 the phases that specify the (Fourier-space forms) of the space groups of ordinary periodic crystals. The space groups were enumerated in Fourier space, as part of a more general derivation for axial quasicrystals of the trigonal type (rotational symmetry n a power of an odd prime) or hexagonal type (n twice a power of an odd prime), by Rabson, Mermin, Rokhsar, and Wright[6, henceforth RMRW]. The phase functions that specify the Fourier-space forms can also be straightforwardly extracted from the more conventional description in the *International Tables*, as noted below.

3.3.1 Hexagonal and Trigonal Point Groups and their Generators

These are listed in Table 3.1. The generators are an n-fold rotation r (where n is 6 or 3), an n-fold roto-inversion $\bar{r} = ir$ (where i is the three-dimensional inversion),

a horizontal mirror h whose invariant plane is perpendicular to the the n-fold axis, a vertical mirror m whose invariant plane includes the n-fold axis, and a 2-fold (dihedral) axis d perpendicular to the the n-fold axis. On the hexagonal P lattice the invariant planes of the vertical mirrors or the axes of the 2-fold rotations can be oriented either along or between the 6-fold star formed by the generating vectors of the triangular horizontal sublattice and their negatives. On the trigonal R lattice vertical mirrors must be between star vectors and 2-fold axes must be along them.

3.3.2 Hexagonal and Trigonal rank-4 Bravais Classes

Periodic crystals have two Bravais classes of rank-3 lattices with a unique axis of 6- or 3-fold symmetry. We review the derivation of this fact in the periodic case, since essentially the same argument works for the Bravais classes of rank-4 lattices of quasiperiodic crystals with such axes.

It follows from the existence of a 3-fold axis that any such rank-3 lattice must be reducible and contain a 2-dimensional ("horizontal") triangular sublattice of vectors perpendicular to the ("vertical") 3-fold axis, that is independently invariant under the point group. We generate the triangular sublattice with two primitive vectors, $\mathbf{a}$ and $\mathbf{b}$, of equal length, separated by 120 degrees. If the third generating vector $\mathbf{c}$ is parallel to the 3-fold axis, we have a lattice of the hexagonal P ("primitive") type with a 6-fold axis. The point group of such a lattice is $\frac{6}{m}\frac{2}{m}\frac{2}{m} = 6/mmm$. We call $\mathbf{c}$ a *vertical stacking vector*, since the P lattice can be viewed as a vertical stacking of horizontal planes containing 2-dimensional triangular lattices. If the third generating vector has both a vertical component $\mathbf{c}$ and a non-zero horizontal component $\mathbf{h}$, then the planes of triangular lattices are stacked with a *staggered stacking vector*,[5]

$$\mathbf{c_s} = \mathbf{c} + \mathbf{h} \ . \tag{3.7}$$

Because $\mathbf{c_s}$ must differ from its 120 degree rotation by a vector in the horizontal sublattice, one easily shows that to within a horizontal lattice vector there are just two choices for the horizontal shift:

$$\mathbf{h} = \pm(\tfrac{2}{3}\mathbf{a} + \tfrac{1}{3}\mathbf{b}) \ . \tag{3.8}$$

These choices are related by a rotation of the whole lattice by 180 degrees which leaves the horizontal sublattice invariant, and are therefore equivalent. There is thus a unique type of staggered stacking, which gives a lattice of the R ("rhombohedral") type. The horizontal component of $\mathbf{c_s}$ reduces the symmetry of the R lattice to 3-fold, with point group $\bar{3}\frac{2}{m} = \bar{3}m$.

In the rank-4 quasiperiodic case, just as in the rank-3 periodic case, one establishes that any such lattice must contain a 2-dimensional triangular sublattice

[5]Vertical and staggered stackings of 2-dimensional lattices were used by Mermin, Rabson, Rokhsar, and Wright[5] to enumerate the Bravais classes of standard axial quasicrystals.

perpendicular to the 3-fold axis, so we can again use **a** and **b** as two of the four lattice generating vectors. Only when the rank is 5 or higher there can be more than one rank-2 horizontal sublattice. For the lattice to be of rank 4 the two remaining generating vectors must both have non-zero incommensurate components parallel to the 3-fold axis, so we have two stacking vectors instead of one. As in the rank-3 case, since each stacking vector must differ from its 120 degree rotation by a vector in the horizontal sublattice, the horizontal component of each can again be taken to be either 0 or $\pm(\frac{2}{3}\mathbf{a}+\frac{1}{3}\mathbf{b})$. Thus to enumerate the trigonal and hexagonal rank-4 Bravais classes we need only examine the different possibilities for the horizontal components of the two stacking vectors.

When both stacking vectors are vertical we have a vertical-vertical lattice, which is a member of a Bravais class we call VV (or V^2). When one stacking vector is vertical and the other has a non-zero horizontal component, we have a staggered-vertical lattice which is a member of a Bravais class we call SV. As in the periodic case, the 6-fold symmetry of the 2-dimensional triangular lattice is reduced to 3-fold by the existence of a staggered stacking vector. Also as in the periodic case, it does not matter which of the two possible non-zero horizontal components in (3.8) is taken for the staggered stacking vector.

A third possibility might appear to arise when both stacking vectors are staggered. But if the two stacking vectors have the same horizontal component **h** then we can reexpress the lattice in the SV form by replacing one of them by the difference of the two, which is a vertical stacking vector; if the stacking vectors have horizontal components that differ in sign, then we can replace one of the staggered stacking vectors by the sum of the two. Thus the SS case is equivalent to the SV case and is not a distinct Bravais class of its own.

The hexagonal VV Bravais class was called hexagonal $P+1$ in Chapter 2, a name which expresses it as a trivial extension of a rank-3 hexagonal P lattice. Here we use the name VV which expresses its full reducibility (in this case also decomposability) into one rank-2 triangular lattice in the horizontal plane (not explicit in the symbol) and two rank-1 lattices generated by two vertical stacking vectors. This nomenclature generalizes to the case of arbitrary rank, studied in Chapter 4. It is clear that the VV Bravais class has only a single setting for the description of modulated crystals in which the rank-3 sublattice of main reflection is generated by the rank-2 horizontal sublattice and one of the vertical stacking vectors.

The trigonal SV Bravais class was called trigonal $R+1$ in Chapter 2, a name which expresses it as a trivial extension of a rank-3 trigonal (rhombohedral) R lattice. The name SV, which generalizes to the case of arbitrary rank, expresses its full reducibility, which in this case is not the same as its decomposability. The rank-2 horizontal sublattice is independently invariant under the point group but together with the staggered stacking vector generates an indecomposable rank-3 rhombohedral lattice. The vertical stacking vector generates an additional a rank-1

Table 3.2: The two rank-4 hexagonal and trigonal Bravais classes, together with their corresponding point groups and their (3+1) settings used to describe modulated crystals. The JJdW symbols for these settings are given in the last column. This table is extended to a larger table in Chapter 4 which deals with lattices of arbitrary finite rank and explicitely list all hexagonal and trigonal Bravais classes up to rank 7 together with their settings associated with different choices of rank-3 sublattices of main reflections.

Bravais Class	**Point Group**	**(3+1) Settings**	**JJdW Symbol**
$SV \quad [R+1]$	$\bar{3}m$	$R,\ P$	$R\bar{3}m(00\gamma),\ P\bar{3}1m(\frac{1}{3}\frac{1}{3}\gamma)$
$VV \quad [P+1]$	$6/mmm$	P	$P6/mmm(00\gamma)$

lattice along the 3-fold axis. Thus the SV Bravais class is 3+1 decomposable and 2+1+1 reducible. From its reducible form one can easily construct its settings for modulated crystals. One can construct an invariant rank-3 sublattice by taking the rank-2 horizontal sublattice along with the staggered stacking vector and generating a rank-3 R lattice, or by taking the rank-2 horizontal sublattice along with the vecrtical stacking vector and generating a P sublattice.

The trigonal and hexagonal rank-4 Bravais classes are summarized in Table 3.2 along with their settings for describing modulated crystals.

3.3.3 Hexagonal and Trigonal Space Groups for Periodic Crystals

RMRW[6] show that there is always a gauge (a choice of real space origin in the periodic case) in which all phase functions are zero on the 2-dimensional triangular sublattice, which is common to lattices in both the P and the R Bravais classes. They also show that in this gauge the only possible non-zero phase functions for the point group generators in Table 3.1 are those associated with the generators r and m. The classes of phase functions can therefore be specified by at most two phases: the values of Φ_r and Φ_m at the stacking vector. These depend on whether the stacking vector is vertical or staggered, and are summarized in Table 3.3 for a vertical stacking vector (P lattice) and in Table 3.4 for a staggered stacking vector (R lattice).

Both tables list for each point group the possible values of the nontrivial phase functions at the stacking vector. They compactly summarize all the gauge equivalence classes of phase functions for the hexagonal and trigonal point groups in the periodic case. To confirm that distinct phases correspond to distinct gauge-equivalence classes of phase functions, note that in every case the phases are given at a vector that is invariant under the corresponding point group generator. They are therefore unaltered by a gauge transformation (3.4).

Table 3.3: Phase functions at generating vectors of the rank-3 P lattice with hexagonal or trigonal point groups. It is enough to specify the phase functions for the point group generators, and their values ("phases") at the primitive lattice-generating vectors. A gauge is used in which all such unspecified phases are zero; the only possible non-zero phases are at the vertical stacking vector $\mathbf{c}$. Point groups with identical phase functions are collected together above the same set of entries. The point groups $\bar{6}2m, \bar{3}m, 3m$, and 32 are listed in two forms, associated with the two possible orientations of the 2-fold axis or vertical mirror. (An m in the second position or a 2 in the third position means the plane of the mirror or the dihedral axis is oriented along the directions of the 6-fold star of horizontal reciprocal lattice generating vectors and their negatives; an m in the third position or a 2 in the second position means the orientation is between star vectors.) These phases are given in Table IV of RMRW[6]. They can also be extracted directly from the *International Tables* by noting that a glide plane corresponds to a value of $\frac{1}{2}$ for the mirror phase function, and that an n_j screw axis corresponds to a value $\frac{j}{n}$ for the rotation phase function. The phases are gauge-invariant since $[m-1]\mathbf{c}$ and $[r-1]\mathbf{c}$ are zero. There are 27 hexagonal and 18 trigonal classes of phase functions, corresponding to the same number of space groups if one distinguishes between enantiomorphic pairs.

G	$\bar{6}$ $\bar{3}$	6 622	3 312 321	$62m$ $31m$ $31m$ $\bar{6}m2$ $\bar{3}m1$ $3m1$	$6/m$	$6mm$ $6/mmm$
Phases	—	$\Phi_r(\mathbf{c})$	$\Phi_r(\mathbf{c})$	$\Phi_m(\mathbf{c})$	$\Phi_r(\mathbf{c})$	$\Phi_r(\mathbf{c})$ $\Phi_m(\mathbf{c})$
Gauge Equivalence Classes		0 $\frac{1}{6}$ $\frac{2}{6}$ $\frac{3}{6}$ $\frac{4}{6}$ $\frac{5}{6}$	0 $\frac{1}{3}$ $\frac{2}{3}$	0 $\frac{1}{2}$	0 $\frac{1}{2}$	0 0 $\frac{1}{2}$ $\frac{1}{2}$

Table 3.4: Phase functions at generating vectors of the rank-3 R lattice with trigonal point groups. A gauge is used in which all unspecified phases are zero. The possible non-zero phases are at a staggered stacking vector $\mathbf{c_s} = \mathbf{c}+\mathbf{h}$. These results are given in Table VI of RMRW[6]. They can also be extracted from the *International Tables* by noting that a glide plane corresponds to having a value of $\frac{1}{2}$ for the mirror phase function. The phases associated with m are gauge-invariant since $[m-1]\mathbf{c_s} = 0$. There are 7 classes of phase functions, corresponding to 7 trigonal space groups on the rank-3 R lattice.

G	$\bar{3}$	$3 \quad 32$	$\bar{3}m \quad 3m$
Phases	—	—	$\Phi_m(\mathbf{c_s})$
Gauge Equivalence Classes			0 $\frac{1}{2}$

These gauge-equivalence classes correspond precisely (for reasons noted below) to the 52 hexagonal and trigonal space groups for periodic crystals. To recognize that they contain nothing but familiar information, note that in the conventional nomenclature of crystallography the tables simply specify the possibility of having a glide plane ($\Phi_m = \frac{1}{2}$, which turns the m into a c in the space group symbol), and/or having a screw axis ($\Phi_r \neq 0$, which adds an appropriate subscript to the 6 or the 3).

Given the gauge-equivalence classes, we arrive at the space groups themselves by eliminating possible redundancies in description arising from the scale equivalence of distinct gauge-equivalence classes. One can verify from Tables 3.3 and 3.4 that the only operations s not in the point group that can leave the lattice invariant and connect different gauge-equivalence classes through (3.6), are improper operations which can do the trick for some of the 3- and 6-fold screw axes. If one adopts the convention that improper operations do not make distinct gauge-equivalence classes scale-equivalent[6] then the gauge-equivalence classes in Tables 3.3 and 3.4 coincide with the space groups, of which there are 27 in the hexagonal system and 25 (18 on the P lattice and 7 on the R lattice) in the trigonal system.

If one allows improper operations to establish scale equivalence then by taking s to be the inversion i one can establish scale equivalence between the gauge-equivalence classes specified by the phases $\Phi_r(\mathbf{c}) \equiv \frac{1}{3}$ and $\frac{2}{3}$ (and similarly between $\frac{1}{6}$ and $\frac{5}{6}$ and between $\frac{2}{6}$ and $\frac{4}{6}$). Of the 11 enantiomorphic pairs of rank-3 space groups four occur in the hexagonal and three in the trigonal crystal systems.

[6]This is the convention that takes enantiomorphic pairs of space groups to be distinct, giving 230 space groups for periodic crystals.

3.4 Phase Functions for the rank-4 Bravais Classes

Due to the decomposability of the Bravais classes, the gauge-equivalence classes of phase functions can be read off directly from Tables 3.3 and 3.4 which list them for the lower-rank constituents. On every constituent sublattice we use the same gauge as used by RMRW in the periodic case and therefore again require only two phase functions, Φ_r and Φ_m. Lattices in the two rank-4 Bravais classes contain altogether three types of lower-rank constituents in their decomposition:[7]

1. Rank-1 lattices along the axis of 3-fold or 6-fold rotation. These are generated by vertical stacking vectors and are contained twice in each VV latice and once in each SV lattice. The phases on the generators of these lattices can be taken directly from Table 3.3 which lists them for the corresponding rank-1 lattice which appears in the decomposition of the rank-3 P lattice.

2. Rank-2 triangular lattices in the horizontal plane are contained once in the decomposition of the VV lattices. Using the same gauge as used by RMRW for the rank-3 hexagonal P lattice, we take all phase functions to be zero on this sublattice.

3. Rank-3 rhombohedral lattices, generated by a triangular lattice in the horizontal plane together with a staggered stacking vector. These appear once in the decomposition of the SV lattices. The phases on the generators of the rank-3 rhombohedral sublattice can be taken directly from Table 3.4. We use the RMRW gauge which sets to zero all the phase functions in the horizontal plane, so that the only non-zero phases are assigned to the stacking vector.

The rank-4 hexagonal and trigonal guage-equivalence classes, constructed in this way, are summarized in Parts I of Tables 3.5–3.7.

3.5 The Hexagonal and Trigonal Rank-4 Space Groups

The further identification of gauge-equivalence classes on the basis of their scale-equivalence, which yields the final space group classification, is to some extent a matter of convention, as already noted in the periodic case, where enantiomorphic space groups are identified only if improper transformations s are allowed in the relation (3.6) between scale-equivalent phase functions. The convention we adopt is to require there to be an interpolating sequence of structures, all with the same point group and rank, between structures belonging to the original and the transformed gauge-equivalence classes. This convention requires the transformations s

[7] We shall show in Chapter 4 that these are the only types of constituents appearing in the decomposition of any hexagonal or trigonal lattice of arbitrary finite rank.

Table 3.5: Gauge-equivalence classes and space groups of rank-4 for the hexagonal system, and their settings for modulated crystals.

The gauge-equivalence classes are given in part I of the Table. They are specified by a set of "phases": the values of a set of phase functions, one for each point group generator, at the primitive generating vectors of the lattice. A gauge is used in which all phases unspecified in the table are zero. The possible non-zero phases are only at the vertical stacking vectors $\mathbf{c}$ and $\mathbf{c}'$ and only associated with the 6-fold rotation r or the vertical mirror m. As discussed in section 3.4, this part of the table is constructed by simply repeating twice (once for $\mathbf{c}$ and once for $\mathbf{c}'$) the information from Table 3.3, which gives the gauge-equivalence classes for the corresponding rank-3 periodic crystals. There are a total of 117 hexagonal rank-4 gauge-equivalence classes: 1 for the point group $\bar{6}$; 36 (6^2) for each of the point groups 6 and 622; 4 (2^2) for the point group $\bar{6}2m$ in each of its two settings and the point group $6/m$; and 16 (2^4) for each of the point groups $6mm$ and $6/mmm$.

Part II of the Table lists the rank-4 space groups arrived at by identifying scale-equivalent gauge-equivalence classes as described in section 3.5. Phases characterizing a given space group are on a horizontal row, enclosed in brackets [...]. (The absence of such brackets in part I of the table indicates that any selection of phases, one from each column, gives a distinct gauge-equivalence class.) In all but the fifth case in the right hand column, the phases at the second stacking vector, $\mathbf{c}'$, can be taken to be zero. There are a total of 25 rank-4 space groups in the hexagonal system.

Part III of the Table lists the different settings of the space groups in the modulated case, where one singles out the rank-3 sublattice of main reflections. We take $\mathbf{c}$ to be the generator of the lattice of main reflections and $\mathbf{c}'$ to describe a satellite peak. The settings are separated vertically into sets that correspond to settings of the general space groups listed in the same order directly above. The 25 rank-4 general space groups subdivide into 54 settings, which correspond to the 54 JJdW (3+1) hexagonal superspace groups. (See Janssen *et al.*[6, pages 823-824].) The JJdW symbols for these settings are constructed by taking the letter P—indicating a P sublattice of main reflections—followed by the point group where (as in the usual notation for periodic crystals) the letter m is changed to c if $\Phi_m(\mathbf{c}) = 1/2$ and the 6 acquires a subscript j if $\Phi_r(\mathbf{c}) = j/6$. This is followed by (00γ)—indicating a vertical (as opposed to staggered) generator for the satellite peaks—followed by the phases at $\mathbf{c}'$ associated with each of the point group generators appearing in the point group symbol (in the order they appear in that symbol), where s means 1/2, t means 1/3, and h means 1/6. For example, the three settings of the fifth space group for point group $6/mmm$ (the group of three entries in the extreme lower right of the Table) have the JJdW symbols $P6/mmc(00\gamma)s000$, $P6_3/mmm(00\gamma)000s$ and $P6_3/mmc(00\gamma)s000$.

G	$\bar{6}$	$6 \quad 622$	$\bar{6}2m$ $\bar{6}m2$	$6/m$	$6mm \qquad 6/mmm$
Phases	—	$\Phi_r(\mathbf{c})\Phi_r(\mathbf{c}')$	$\Phi_m(\mathbf{c})\Phi_m(\mathbf{c}')$	$\Phi_r(\mathbf{c})\Phi_r(\mathbf{c}')$	$\Phi_r(\mathbf{c})\Phi_m(\mathbf{c}) \quad \Phi_r(\mathbf{c}')\Phi_m(\mathbf{c}')$
I. Gauge Equivalence Classes		$0 \quad 0$ $\frac{1}{6} \quad \frac{1}{6}$ $\frac{2}{6} \quad \frac{2}{6}$ $\frac{3}{6} \quad \frac{3}{6}$ $\frac{4}{6} \quad \frac{4}{6}$ $\frac{5}{6} \quad \frac{5}{6}$	$0 \quad 0$ $\frac{1}{2} \quad \frac{1}{2}$	$0 \quad 0$ $\frac{1}{2} \quad \frac{1}{2}$	$0 \quad 0 \quad 0 \quad 0$ $\frac{1}{2} \quad \frac{1}{2} \quad \frac{1}{2} \quad \frac{1}{2}$
II. General rank-4 Space Groups		$[\,0 \quad 0\,]$ $[\,\frac{1}{6} \quad 0\,]$ $[\,\frac{2}{6} \quad 0\,]$ $[\,\frac{3}{6} \quad 0\,]$	$[\,0 \quad 0\,]$ $[\,\frac{1}{2} \quad 0\,]$	$[\,0 \quad 0\,]$ $[\,\frac{1}{2} \quad 0\,]$	$[\,0 \quad 0 \quad 0 \quad 0\,]$ $[\,\frac{1}{2} \quad 0 \quad 0 \quad 0\,]$ $[\,0 \quad \frac{1}{2} \quad 0 \quad 0\,]$ $[\,\frac{1}{2} \quad \frac{1}{2} \quad 0 \quad 0\,]$ $[\,0 \quad \frac{1}{2} \quad \frac{1}{2} \quad 0\,]$
III. Settings of General Space Groups for Modulated Crystals		$[\,0 \quad 0\,]$ $[\,\frac{1}{6} \quad 0\,]$ $[\,\frac{2}{6} \quad \frac{1}{6}\,]$ $[\,\frac{3}{6} \quad \frac{1}{6}\,]$ $[\,\frac{4}{6} \quad \frac{1}{6}\,]$ $[\,\frac{5}{6} \quad 0\,]$ $[\,0 \quad \frac{1}{6}\,]$ $[\,\frac{2}{6} \quad 0\,]$ $[\,\frac{4}{6} \quad 0\,]$ $[\,0 \quad \frac{2}{6}\,]$ $[\,\frac{3}{6} \quad 0\,]$ $[\,0 \quad \frac{3}{6}\,]$	$[\,0 \quad 0\,]$ $[\,\frac{1}{2} \quad 0\,]$ $[\,0 \quad \frac{1}{2}\,]$	$[\,0 \quad 0\,]$ $[\,\frac{1}{2} \quad 0\,]$ $[\,0 \quad \frac{1}{2}\,]$	$[\,0 \quad 0 \quad 0 \quad 0\,]$ $[\,\frac{1}{2} \quad 0 \quad 0 \quad 0\,]$ $[\,0 \quad 0 \quad \frac{1}{2} \quad 0\,]$ $[\,0 \quad \frac{1}{2} \quad 0 \quad 0\,]$ $[\,0 \quad 0 \quad 0 \quad \frac{1}{2}\,]$ $[\,\frac{1}{2} \quad \frac{1}{2} \quad 0 \quad 0\,]$ $[\,0 \quad 0 \quad \frac{1}{2} \quad \frac{1}{2}\,]$ $[\,0 \quad \frac{1}{2} \quad \frac{1}{2} \quad 0\,]$ $[\,\frac{1}{2} \quad 0 \quad 0 \quad \frac{1}{2}\,]$ $[\,\frac{1}{2} \quad \frac{1}{2} \quad \frac{1}{2} \quad 0\,]$

Table 3.6: Gauge-equivalence classes and space groups of rank-4 in the trigonal system for the VV $(P+1)$ Bravais class, and their settings for modulated crystals.

The structure and conventions are the same as for Table 3.5. Part I, taken directly from Table 3.3, lists 44 gauge-equivalence classes: one for the point group $\bar{3}$; nine (3^2) for the point group 3 and the point group 32 in each of its two orientations; and four (2^2) for each of the two orientations of each of the two point groups $\bar{3}m$ and $3m$. Part II lists the 15 space groups to which these gauge-equivalence classes reduce under scale-equivalence. In all of these the phases of the second stacking vector, $\mathbf{c}'$, can be taken to be zero. Part III of the table lists the 25 different settings for these space groups in the modulated case. The JJdW superspace symbols are constructed in the same way as specified for the hexagonal space groups in the caption of Table 3.5.

G	$\bar{3}$	3	321 312	$3m1$ $\bar{3}1m$	$3m1$ $31m$
Phases	—	$\Phi_r(\mathbf{c})$	$\Phi_r(\mathbf{c}')$	$\Phi_m(\mathbf{c})$	$\Phi_m(\mathbf{c}')$
I. Gauge-equivalence Classes		0 $\frac{1}{3}$ $\frac{2}{3}$	0 $\frac{1}{3}$ $\frac{2}{3}$	0 $\frac{1}{2}$	0 $\frac{1}{2}$
II. General rank-4 Space Groups		$[\ 0\ \ 0\ ]$ $[\ \frac{1}{3}\ \ 0\ ]$		$[\ 0\ \ 0\ ]$ $[\ \frac{1}{2}\ \ 0\ ]$	
III. Settings of General Space Groups for Modulated Crystals		$[\ 0\ \ 0\ ]$ $[\ \frac{1}{3}\ \ 0\ ]$ $[\ \frac{2}{3}\ \ 0\ ]$ $[\ 0\ \ \frac{1}{3}\ ]$		$[\ 0\ \ 0\ ]$ $[\ \frac{1}{2}\ \ 0\ ]$ $[\ 0\ \ \frac{1}{2}\ ]$	

Table 3.7: Gauge-equivalence classes and space groups of rank-4 in the trigonal system for the SV $(R+1)$ Bravais class, and their settings for modulated crystals.

The structure and conventions are the same as for Table 3.5, except that *(1)* the settings for modulated crystals occupy two sections because the SV lattice itself has two possible settings, and *(2)* the entries in the upper part of the table for the phases at the generating vector $\mathbf{c_s}$ are now the phases for the ordinary rank-3 space groups on the R lattice, taken from Table 3.4. Part I of the table lists 15 gauge-equivalence classes: one for the point group $\bar{3}$; three for each of the point groups 3 and 32; and four (2^2) for each of the two point groups $\bar{3}m$ and $3m$. Part II lists the 9 space groups to which these gauge-equivalence classes reduce under scale-equivalence. In all of these the phases of the second stacking vector, $\mathbf{c}'$, can be taken to be zero. Part III of the table lists the 11 different settings for these space groups in the modulated case when the lattice of main reflections is rhombohedral (R settings), and part IV lists the 13 different settings in the modulated case when the lattice of main reflections is primitive (P settings). The numbers differ because in the P setting the scale-equivalence transformations are required to preserve the rank-3 P sublattice, and one therefore looses the freedom to rescale the $\mathbf{c}'$ axis so as to identify the two enantiamorphic pairs of screw axes. The JJdW superspace symbols are constructed in a manner similar to that specified for the hexagonal space groups in the caption of Table 3.5, taking $R\bar{3}m(00\gamma)$ for the underlying symbol in the R settings, and $P\bar{3}1m(\frac{1}{3}\frac{1}{3}\gamma)$ in the P settings.

G	$\bar{3}$	3 32	$\bar{3}m$	$3m$
Phases	—	$\Phi_r(\mathbf{c}')$	$\Phi_m(\mathbf{c}_s)$	$\Phi_m(\mathbf{c}')$
I. Gauge-equivalence Classes		0	0	0
		$\frac{1}{3}$	$\frac{1}{2}$	$\frac{1}{2}$
		$\frac{2}{3}$		
II. General rank-4 Space Groups		0	[0	0]
		$\frac{1}{3}$	[$\frac{1}{2}$	0]
III. R Settings of General Space Groups for Modulated Crystals		0	[0	0]
		$\frac{1}{3}$	[$\frac{1}{2}$	0]
			[0	$\frac{1}{2}$]
IV. P Settings of General Space Groups for Modulated Crystals		0	[0	0]
		$\frac{1}{3}$	[$\frac{1}{2}$	0]
		$\frac{2}{3}$	[0	$\frac{1}{2}$]

to be sense-preserving and thus maintains the traditional distinction between enantiomorphic pairs in the rank-3 case. We shall find, however, that in the rank-4 case some distinctions between 6_j (or 3_j) screw axes with different values of j can still be lost, just as it is in the icosahedral case (see Rokhsar, Wright, and Mermin[7]).

In section 3.5.1 we describe the general form of the transformations s leading to the scale-equivalence of many of the gauge-equivalence classes in Tables 3.5–3.7. In section 3.5.2 we describe how the forms of these general transformations are restricted if one requires that they preserve a rank-3 sublattice of main reflections, as is useful in describing modulated crystals. This leads to different settings of the general space groups that correspond precisely to the JJdW "superspace groups". In section 3.5.3 we describe in detail how the general transformations of section 3.5.1 lead to the general space groups (given in parts II of Tables 3.5–3.7) and how the restrictions on those transformations in section 3.5.2 lead to the different settings of those space groups for modulated crystals (given in parts III of Tables 3.5 and 3.6 and parts III and IV of Table 3.7).

3.5.1 Scale Equivalence

VV Bravais Class

We take the primitive vectors $\mathbf{c}$ and $\mathbf{c}'$ each to point in the direction of advance of a right–handed screw, rotating through 120 degrees from $\mathbf{a}$ to $\mathbf{b}$. If

$$\begin{pmatrix} t & u \\ v & w \end{pmatrix} \tag{3.9}$$

is a matrix of integers with determinant ± 1 (to ensure that its inverse is also a matrix of integers) that preserves the sense of

$$\begin{aligned} \overline{\mathbf{c}} &= t\mathbf{c} + u\mathbf{c}', \\ \overline{\mathbf{c}'} &= v\mathbf{c} + w\mathbf{c}', \end{aligned} \tag{3.10}$$

then $\overline{\mathbf{c}}$ and $\overline{\mathbf{c}'}$ constitute an entirely equivalent pair of primitive lattice-generating vectors. The orientation-preserving transformation s that scales $\mathbf{c}$ into $\overline{\mathbf{c}}$ and $\mathbf{c}'$ into $\overline{\mathbf{c}'}$ therefore leaves the lattice invariant. It induces the identity transformation on the point group of the lattice, and can therefore lead to a scale-equivalence of distinct gauge-equivalence classes. The transformation (3.6) on the phases is

$$\begin{aligned} \Phi'_g(\overline{\mathbf{c}}) &= t\Phi_g(\mathbf{c}) + u\Phi_g(\mathbf{c}'), \\ \Phi'_g(\overline{\mathbf{c}'}) &= v\Phi_g(\mathbf{c}) + w\Phi_g(\mathbf{c}'). \end{aligned} \tag{3.11}$$

Two gauge-equivalence classes specified by sets of phases related by (3.11) are scale-equivalent, and therefore specify the same space group.

SV **Bravais Class**

We take the same sense convention for $\mathbf{c}'$ and the vertical part of $\mathbf{c_s}$ and consider the sense preserving transformation of primitive stacking vectors $\mathbf{c}$ and $\mathbf{c_s}$ given by

$$\begin{array}{rcl} \overline{\mathbf{c_s}} & = & t\mathbf{c_s} + u\mathbf{c}' - (t-1)\mathbf{h}, \\ \overline{\mathbf{c}'} & = & v\mathbf{c_s} + w\mathbf{c}' - v\mathbf{h}, \end{array} \tag{3.12}$$

where the matrix of integers (3.9) again has determinant ± 1 and where v and $t-1$ are multiples of 3. Recall from (3.8) that $3\mathbf{h}$ is a vector of the horizontal sublattice. These restrictions on v and t ensure that the new pair of stacking vectors can be obtained from the old pair by an orientation preserving transformation that scales $\mathbf{c}'$ and the vertical part of $\mathbf{c_s}$ into $\overline{\mathbf{c}'}$ and the vertical part of $\overline{\mathbf{c_s}}$. Such a rescaling leaves the lattice invariant and induces the identity transformation on the point group of the lattice. Since $3\mathbf{h}$ is a vector of the horizontal sublattice and since all phase functions vanish in the horizontal plane, the terms in $\mathbf{h}$ in (3.12) drop out of the condition (3.6) for scale-equivalence, and we have, as in the case of the VV lattice,

$$\begin{array}{rcl} \Phi'_g(\overline{\mathbf{c_s}}) & = & t\Phi_g(\mathbf{c_s}) + u\Phi_g(\mathbf{c}'), \\ \Phi'_g(\overline{\mathbf{c}'}) & = & v\Phi_g(\mathbf{c_s}) + w\Phi_g(\mathbf{c}'), \end{array} \tag{3.13}$$

with the additional restriction that v and $t-1$ must be multiples of 3.

3.5.2 Restricted Scale Equivalence for Modulated Crystals

To further subdivide the general space groups into their settings for describing modulated crystals we need only note that it is the convention in the modulated case to include among the lattice generating vectors a set of three that generate the sublattice of main reflections, and to restrict the transformations that establish scale-equivalence to those that take this sublattice into itself. In the case of the VV lattice we choose $\mathbf{c}$ to generate the lattice of main reflections together with $\mathbf{a}$ and $\mathbf{b}$. As a result, the matrices (3.9) are acceptable candidates for scale-equivalence in (3.11) only if they are of the restricted form

$$\begin{pmatrix} t & u \\ v & w \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ v & \pm 1 \end{pmatrix}. \tag{3.14}$$

In the case of the SV lattice the restriction on (3.12) depends on whether the R or P rank-3 sublattice is taken as the lattice of main reflections. In the former case it is $\mathbf{c_s}$ that must be preserved and (3.14) again applies (with the restriction that v is a multiple of 3). In the latter case $\mathbf{c}'$ must be preserved and we have

$$\begin{pmatrix} t & u \\ v & w \end{pmatrix} = \begin{pmatrix} \pm 1 & u \\ 0 & 1 \end{pmatrix}. \tag{3.15}$$

3.5.3 Space Groups and Their Settings for Modulated Crystals

VV **Bravais Class**

Case (1). Point groups allowing a glide-plane or a 2-fold screw-axis, but not both. ($\bar{6}2m$, $\bar{6}m2$, $6/m$, $\bar{3}1m$, $\bar{3}m1$, $31m$, $3m1$)

These are the cases in Tables 3.5 and 3.6 for which parts I of the tables give four gauge-equivalence classes of phase functions:

$$\begin{pmatrix} \Phi_g(\mathbf{c}) \\ \Phi_g(\mathbf{c}') \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}, \begin{pmatrix} \frac{1}{2} \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ \frac{1}{2} \end{pmatrix}, \text{ or } \begin{pmatrix} \frac{1}{2} \\ \frac{1}{2} \end{pmatrix}, \tag{3.16}$$

where the point group generator g is either m or r. That the third and fourth classes are scale-equivalent to the second is established by noting that

$$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ \frac{1}{2} \end{pmatrix} \equiv \begin{pmatrix} \frac{1}{2} \\ 0 \end{pmatrix}; \qquad \begin{pmatrix} 1 & 0 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} \frac{1}{2} \\ \frac{1}{2} \end{pmatrix} \equiv \begin{pmatrix} \frac{1}{2} \\ 0 \end{pmatrix}. \tag{3.17}$$

Thus for each point group there is just one non-symmorphic space group, as indicated by the corresponding entries in parts II of Tables 3.5 and 3.6.

To identify the settings of the general space groups appropriate to the modulated case we must restrict the matrices in (3.17) to those of the form (3.14). The first identification in (3.17) is then prohibited, giving two distinct settings for the non-symmorphic space group, as given in parts III of Tables 3.5 and 3.6.

Case (2). Point groups allowing both a glide-plane and a 2-fold screw-axis. ($6mm$, $6/mmm$)

We can now make the choice (3.16) independently both for Φ_m and Φ_r, giving 16 distinct gauge-equivalence classes. If *(a)* both mirror phases are zero, *(b)* both rotational phases are zero, or *(c)* the mirror and rotational phases are the same, then we can repeat the treatment in Case (1): the three non-trivial gauge-equivalence classes in each of the cases *(a)*–*(c)* give a single non-symmorphic space group for each point group, given by the second, third, and fourth entries in the right–hand section of Part II of Table 3.5. These each have two settings in the modulated case, as indicated by the corresponding entries in Part III.

This leaves 6 gauge-equivalence classes in which both phase functions are non-zero but Φ_m is not identical to Φ_r. All 6, however, are easily shown to be scale-

equivalent, under transformations of the form (3.17), to the single class[8]

$$\begin{pmatrix} \Phi_r(\mathbf{c}) \\ \Phi_r(\mathbf{c}') \end{pmatrix} = \begin{pmatrix} 0 \\ \frac{1}{2} \end{pmatrix}, \qquad \begin{pmatrix} \Phi_m(\mathbf{c}) \\ \Phi_m(\mathbf{c}') \end{pmatrix} = \begin{pmatrix} \frac{1}{2} \\ 0 \end{pmatrix}, \tag{3.18}$$

so there is only one additional space group for each point group, listed as a fifth entry in part II of Table 3.5.

These space groups each have three settings in the modulated case, where the matrices establishing scale-equivalence are restricted to the form (3.14) which limits the identifications to those that can be realized with the matrix $\begin{pmatrix} 1 & 0 \\ 1 & 1 \end{pmatrix}$. These are given in the fifth entry of part III of Table 3.5.

Case (3). Point groups allowing a 6-fold or 3-fold screw-axis. (6, 622, 3, 321, 312)

For each point group, the phase function Φ_r can have the values $0, \frac{1}{n}, \ldots, \frac{n-1}{n}$ independently for each of the stacking vectors, giving 36 gauge-equivalence classes of phase functions when $n = 6$, and 9 classes when $n = 3$.

When $n = 6$, it can be shown that the 36 classes reduce to 4 under scale-equivalence: (1) the single symmorphic gauge-equivalence class; (2) any of the 3 non-trivial gauge-equivalence classes in which both phases are integral multiples of $\frac{1}{2}$; (3) any of the 8 non-trivial gauge-equivalence classes in which both phases are integral multiples of $\frac{1}{3}$; (4) any of the 24 remaining gauge-equivalence classes. This follows from the fact that if positive integers t and v are relatively prime, then positive integers u and w can be found such that $tw - uv = 1$. Consequently

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \text{and} \qquad \begin{pmatrix} t \\ v \end{pmatrix} = \begin{pmatrix} t & u \\ v & w \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{3.19}$$

are related by a transformation of the form (3.9) that establishes scale-equivalence. Since categories (2)–(4) have phases that are $\frac{1}{2}$, $\frac{1}{3}$, or $\frac{1}{6}$ times a column vector with two relatively prime integers, we can represent the four space-group categories by:

$$\begin{pmatrix} \Phi_r(\mathbf{c}) \\ \Phi_r(\mathbf{c}') \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}, \begin{pmatrix} \frac{1}{2} \\ 0 \end{pmatrix}, \begin{pmatrix} \frac{1}{3} \\ 0 \end{pmatrix}, \text{ or } \begin{pmatrix} \frac{1}{6} \\ 0 \end{pmatrix}, \tag{3.20}$$

as noted in part II of Table 3.5.

To find the settings appropriate to the modulated case, we prohibit identifications that change the value of $\Phi_r(\mathbf{c})$. This results in two settings in case (2)

[8]The matrix $\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$ interchanges the $\mathbf{c}$ and $\mathbf{c}'$ phases, reducing the number of classes to 3. The matrix $\begin{pmatrix} 1 & 1 \\ 0 & 1 \end{pmatrix}$ then takes $\begin{pmatrix} \frac{1}{2} \\ \frac{1}{2} \end{pmatrix}$, $\begin{pmatrix} \frac{1}{2} \\ 0 \end{pmatrix}$ into $\begin{pmatrix} 0 \\ \frac{1}{2} \end{pmatrix}$, $\begin{pmatrix} \frac{1}{2} \\ 0 \end{pmatrix}$; and the matrix $\begin{pmatrix} 1 & 0 \\ 1 & 1 \end{pmatrix}$ takes $\begin{pmatrix} 0 \\ \frac{1}{2} \end{pmatrix}$, $\begin{pmatrix} \frac{1}{2} \\ \frac{1}{2} \end{pmatrix}$ into $\begin{pmatrix} 0 \\ \frac{1}{2} \end{pmatrix}$, $\begin{pmatrix} \frac{1}{2} \\ 0 \end{pmatrix}$.

($\Phi_r(\mathbf{c}) \equiv 0,\ \frac{1}{2}$), three settings in case (3) ($\Phi_r(\mathbf{c}) \equiv 0,\ \frac{1}{3},\ \frac{2}{3}$), and six settings in case (4) ($\Phi_r(\mathbf{c}) \equiv 0,\ \frac{1}{6}, \ldots \frac{5}{6}$). These are listed with the values of $\Phi_r(\mathbf{c}')$ in part III of Table 3.5.

When $n = 3$, in just the same way, all 8 of the 9 non-trivial gauge-equivalence classes are scale-equivalent, but they have three settings in the modulated case, as shown in Table 3.6.

Note that in the general case the existence of two incommensurate c-axes results in the inability to distinguish between enantiomorphic pairs of screw axes. A similar simplification associated with 5-fold screw axes in icosahedral quasicrystals was pointed out by Rokhsar, Wright, and Mermin[7].

SV **Bravais Class**

In establishing scale-equivalence of the non-symmorphic space groups we are now restricted to matrices (3.9) in which v and $t - 1$ must be multiples of 3.

Case (1). Point groups that allow a glide-plane. ($\bar{3}m$, $3m$)

From part I of Table 3.7 we see that for each point group there are four gauge-equivalence classes,

$$\begin{pmatrix} \Phi_m(\mathbf{c_s}) \\ \Phi_m(\mathbf{c}') \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix},\ \begin{pmatrix} 0 \\ \frac{1}{2} \end{pmatrix},\ \begin{pmatrix} \frac{1}{2} \\ 0 \end{pmatrix},\ \text{or}\ \begin{pmatrix} \frac{1}{2} \\ \frac{1}{2} \end{pmatrix}. \tag{3.21}$$

Scale-equivalence between the three non-trivial ones can be established by the transformations:

$$\begin{pmatrix} 1 & 1 \\ 3 & 2 \end{pmatrix} \begin{pmatrix} 0 \\ \frac{1}{2} \end{pmatrix} \equiv \begin{pmatrix} \frac{1}{2} \\ 0 \end{pmatrix},\quad \begin{pmatrix} 1 & 0 \\ 3 & 1 \end{pmatrix} \begin{pmatrix} \frac{1}{2} \\ \frac{1}{2} \end{pmatrix} \equiv \begin{pmatrix} \frac{1}{2} \\ 0 \end{pmatrix}. \tag{3.22}$$

For each point group there is therefore just one non-symmorphic space group as listed in part II of Table 3.7.

To further subdivide these space groups into the settings appropriate to the modulated case note first that there is a general doubling of categories depending on whether the sublattice of main reflections is taken to be P or R, so that even the symmorphic space groups have two different settings. Each non-symmorphic space group has four settings: if the lattice of main reflections is R then the assignment of phases 0 or $\frac{1}{2}$ to $\mathbf{c_s}$ must be distinguished, while if it is P, one must distinguish the same two assignments to $\mathbf{c}'$. This is indicated in parts III and IV of Table 3.7.

Case(2). Point groups that allow a 3-fold screw-axis. (3, 32)

For each point group there are three gauge-equivalence classes,

$$\begin{pmatrix} \Phi_r(\mathbf{c_s}) \\ \Phi_r(\mathbf{c}') \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix},\ \begin{pmatrix} 0 \\ \frac{1}{3} \end{pmatrix},\ \text{or}\ \begin{pmatrix} 0 \\ \frac{2}{3} \end{pmatrix}. \tag{3.23}$$

Scale-equivalence between the two non-trivial phases is established by the transformation

$$\begin{pmatrix} 0 \\ \frac{2}{3} \end{pmatrix} \equiv \begin{pmatrix} 1 & 0 \\ v & -1 \end{pmatrix} \begin{pmatrix} 0 \\ \frac{1}{3} \end{pmatrix}, \tag{3.24}$$

where v is a multiple of 3 large enough to preserve the sense of $\mathbf{c}'$. Here too, it is not possible to distinguish between enantiomorphic pairs of space groups.

In the modulated case there continues to be a single non-symmorphic space group in the R setting, but in the P setting the phases of $\mathbf{c}'$, $\frac{1}{3}$ and $\frac{2}{3}$, are associated with the lattice of main reflections and therefore cannot be identified.

Bibliography

[1] Janner, A., T. Janssen, and P. M. de Wolff, "Bravais classes for incommensurate crystal phases", *Acta Cryst.* A**39** (1983) 658–666.

[2] T. Janssen, A. Janner, A. Looijenga-Vos, and P. M. de Wolff, "Incommensurate and commensurate modulated structures". *International Tables for Crystallography, Volume C.*, ed. A. J. C. Wilson (Kluwer Academic, Dodrecht, 1992) 797–844.

[3] N. D. Mermin, "The space groups of icosahedral quasicrystals and cubic, orthorhombic, monoclinic and triclinic crystals", *Revs. Mod. Phys.* **64** (1992) 3–49.

[4] N. D. Mermin and R. Lifshitz, "The Bravais classes for the simplest incommensurate crystal phases", *Acta Cryst.* A**48** (1992) 515–532.

[5] N. D. Mermin, D. A. Rabson, D. S. Rokhsar, and D. C. Wright, "Stacking quasicrystallographic lattices", *Phys. Rev.* B**41** (1990) 10498–10502.

[6] D. A. Rabson, N. D. Mermin, D. S. Rokhsar, and D. C. Wright, "The space groups of axial crystals and quasicrystals", *Revs. Mod. Phys.* **63** (1991) 699–733.

[7] D. S. Rokhsar, D. C. Wright, and N. D. Mermin, "Scale equivalence of quasicrystallographic space groups", *Phys. Rev.* B**37** (1988) 8145–8149.

[8] P. M. de Wolff, T. Janssen, and A. Janner, "The superspace groups for incommensurate crystal structures with a one-dimensional modulation", *Acta Cryst.* A**37** (1981) 625–636.

[9] A. Yamamoto, T. Janssen, A. Janner, and P. M. de Wolff, "A note on the superspace groups for one-dimensionally modulated structures", *Acta Cryst.* A**41** (1985) 528–530.

Chapter 4

Bravais Classes and Space Groups for Trigonal and Hexagonal Quasiperiodic Crystals of Arbitrary Finite Rank

4.1 Introduction

We show here that a modest extension of the analysis in Chapter 3 yields the Bravais classes and space groups for trigonal and hexagonal quasiperiodic crystals of arbitrary finite rank. We describe the rank-n Bravais classes in section 4.2, deriving them in Appendix A. We derive the space groups associated with each Bravais class in section 4.3.

The possible subdivisions of space groups and Bravais classes into settings that identify different sublattices of wave vectors as lattices of main reflections are much more extensive than in the rank-4 case, since there are no longer any *a priori* grounds for restricting lattices of main reflections to rank-3 sublattices. If, for example, we wished to consider the categories of rank-5 quasiperiodic crystals with weak satellites requiring two additional vectors for their indexing, these would be given by the (5+2) settings of the general rank-7 space groups. It is straightforward to extract these settings for any case of interest. We illustrate how to do this in section 4.4 for the important case of rank-3 lattices of main reflections, recovering the "Bravais classes for incommensurate crystal phases" of Janner, Janssen, and de Wolff[1, henceforth JJdW] for ranks 4 to 6, and deriving their generalizations to any arbitrary finite rank. We also derive the (3+d) settings of the space groups extending the tabulated "superspace groups for incommensurate crystal structures with a one-dimensional modulation" of de Wolff, Janner, and Janssen[3,2] for the trigonal and hexagonal crystal systems, to modulations of any finite rank.

4.2 Bravais Classes

We follow the 3-dimensional geometric approach used in section 3.3.2, describing the Bravais classes in terms of a 2-dimensional horizontal sublattice H of wave vectors perpendicular to the 3-fold (or 6-fold) axis, and in terms of stacking vectors. We first describe the Bravais classes of 2-dimensional lattices with 6-fold symmetry that can be horizontal sublattices of the full 3-dimensional lattice. These Bravais classes are clearly distinct if we follow our definition in section 2.2.2 in taking classes to be distinct if it is impossible to interpolate between them through a sequence of lattices all with the same point group and rank. In Appendix A (sections A.1 and A.2) we prove that there are no additional Bravais classes.

4.2.1 The horizontal sublattice

The 2-dimensional horizontal sublattice H is primitively generated by pairs of wave vectors $\mathbf{a}_i$ and $\mathbf{b}_i$, of equal length, separated by 120 degrees. Each such pair generates a 6-fold star of vectors given by $\pm\mathbf{a}_i, \pm\mathbf{b}_i$, and $\pm(\mathbf{a}_i + \mathbf{b}_i)$.

Symmetry distinguishes two ways of orienting the stars:

(a) If every star has the same orientation, or if each star has one of two orientations, separated by 30 degrees, then the 2-dimensional horizontal sublattice is invariant under the full 3-dimensional point group $6/mmm$. We say that such sublattices are of type $[i, j]$ where i and j are even integers giving the number of primitive vectors in the plane generating stars of each orientation. The rank of the horizontal sublattice is then $i+j$. We include a single set of star directions in the case $[i, 0]$.

(b) If there is at least one pair of stars separated by an angle less than 30 degrees then the symmetry of the 2-dimensional sublattice is reduced to $6/m$. One can interpolate between any two such sublattices having the same number of stars without any change of symmetry. Consequently any relations between the orientations of any other stars in the family is accidental. The types of sublattices are now distinguished only by the total number of primitive vectors in the plane. We denote horizontal sublattices of this type by the symbol $[i]$, with i an even number greater than two, giving the rank of the sublattice.

Three-dimensional hexagonal or trigonal lattices with horizontal sublattices of distinct types obviously belong to distinct Bravais classes. Further subdivisions of the Bravais classes for the full lattice are determined by the additional primitive generating vectors with non-zero vertical components—the stacking vectors.

4.2.2 Stacking vectors

As in the periodic (rank-3) case, the stacking vectors can be either vertical or staggered. We show in Appendix A (section A.3) that primitive generating vectors

can always be chosen so that the horizontal shift of a staggered stacking vector has the form

$$\mathbf{h}_i = \tfrac{2}{3}\mathbf{a}_i + \tfrac{1}{3}\mathbf{b}_i \ , \tag{4.1}$$

where $\mathbf{a}_i$ and $\mathbf{b}_i$ are one of the pairs of primitive generators of the horizontal sublattice.

If all stacking vectors are vertical, the point group of the full lattice remains that of the 2-dimensional sublattice: $6/mmm$ if the 2-dimensional sublattice is of type $[i,j]$ and $6/m$ if it is of type $[i]$. The full Bravais class is then determined by the type of the horizontal sublattice and the total number of vertical stacking vectors.

If there are staggered stacking vectors, then as in the rank-4 case one requires at most one for each pair of horizontal generating vectors. When the 2-dimensional sublattice is of the type $[i,j]$, the existence of just one staggered stacking vector reduces the rotational symmetry to 3-fold and removes one of the mirrors, reducing the point group of the full lattice to $\bar{3}m$. The vertical mirror that remains still provides enough symmetry to maintain the stars in just two orientations, since an infinitessimal rotation of any one star would further reduce the symmetry to $\bar{3}$. The $\bar{3}m$ symmetry is preserved by additional stacking vectors, provided their horizontal shifts are all associated through (4.1) with stars of the same orientation. If, however, there are two staggered vectors with horizontal shifts associated with stars of different orientations, then the point group is reduced to $\bar{3}$, and there are no longer symmetry-based grounds for the stars to have just two orientations. Thus when stacking 2-dimensional lattices of the type $[i,j]$, staggered stacking vectors can be associated with only one of the groups of stars. If an attempt is made to associate staggered vectors with stars from both groups, then the 2-dimensional sublattice $[i,j]$ will be unstable against a deformation to type $[\,i+j\,]$.

4.2.3 Hexagonal and trigonal Bravais classes — summary

In summary, (see Table 4.1) the Bravais classes of hexagonal and trigonal crystals of arbitrary finite rank are characterized as follows:

(a) *Horizontal sublattice of type* $[i,j]$: The horizontal primitive vectors give stars of no more than two orientations, 30 degrees apart. We identify the Bravais class by the symbol $[i,j]S^kV^l$, where i and j are the (even) numbers of horizontal sublattice generating vectors giving stars in each orientation, and k and l are the numbers of staggered and vertical stacking vectors. If k or l are 0, we omit the S or V from the symbol.[1] If there are no staggered stacking vectors then we may take $i \geq j$. If there are staggered stacking vectors then all must be associated with stars of the same orientation, and we adopt the convention that these stars are given by the first group of i horizontal generating vectors

[1]The symbol $[i,j]$ is omitted in the discussion in Chapter 3 of the rank-3 and rank-4 cases because it is always $[2,0]$.

Table 4.1: The hexagonal and trigonal Bravais classes of arbitrary finite rank and their point groups. The notation is explained in section 4.2. When the horizontal sublattice is of type $[i, j]$ our convention is that i is associated with the staggered stacking vectors if there are any, and $i \geq j$ otherwise. If there are no staggered stacking vectors and the horizontal sublattice is of type $[i, j]$ then the lattice has the full hexagonal point group $6/mmm$. The existence of staggered stacking vectors reduces the rotational symmetry to 3-fold and removes one of the vertical mirrors. Horizontal sublattices of type $[i]$ have no vertical mirror symmetry.

Bravais class	$[i, j]S^kV^l$	$[i]S^kV^l$
No staggered stacking vectors ($k = 0$)	$6/mmm$	$6/m$
At least one staggered stacking vector ($k > 0$)	$\bar{3}m$	$\bar{3}$

in the square brackets (so that $k \leq \frac{1}{2}i$). The symmetry of the full lattice is $6/mmm$ if staggered stacking vectors are absent, and $\bar{3}m$ if they are present. The rank is $n = i+j+k+l$.

(b) Horizontal lattice of type $[i]$: The horizontal primitive vectors give stars with unrelated orientations (so there must be at least two stars). We identify the Bravais class by the symbol $[i]S^kV^l$, where $i \geq 4$ is the (even) number of horizontal sublattice generating vectors, $k \leq \frac{1}{2}i$ is the number of staggered stacking vectors, and l is the number of vertical stacking vectors. The symmetry of the full lattice is $6/m$ if there are no staggered stacking vectors, and $\bar{3}$ if there are. The rank is $n = i+k+l$.

The enumeration of these possibilities for any given rank n is straightforward, and is illustrated in the first 2 columns of Table 4.2 which lists the trigonal and hexagonal Bravais classes from rank 3 to rank 7.

Table 4.2: An explicit catalog of the Bravais classes of trigonal and hexagonal lattices for ranks 3–7, and their (3+d) settings.

The table of Bravais classes for arbitrary rank-n is constructed by simply enumerating the cases in section 4.2 for which $i+j+k+l = n$. The (3+d) settings are found by applying the general rules of section 4.4.1 and Table 4.6. The Bravais classes are grouped in the table by their rank and further subgrouped by the number of generating vectors in the horizontal sublattice (or equivalently, by the number of incommensurate stacking vectors). The first column lists the Bravais classes using the notation $[i,j]S^kV^l$ or $[i]S^kV^l$ described in section 4.2. The second column gives the point group of the lattices in each Bravais class according to the general rules of Table 4.1. The third column lists the possible (3+d) settings useful in describing incommensurately modulated periodic crystals. The notation for the different settings is described in section 4.4.1 and summarized in Table 4.6. The last column lists the same settings using the superspace notation of JJdW[1] where they are characterized as "(3+d) Bravais classes", and listed up to rank-6. We have made the obvious generalization of the JJdW notation to rank-7, but do not recomend it. In Chapter 2 we used the symbols SV or $R+1$ and VV or $P+1$ for the two rank-4 Bravais classes.

Bravais Class	**Point Group**	**(3+d) Settings**	**JJdW Symbol**
		rank-3	
$[2,0]S[R]$	$\bar{3}m$		
$[2,0]V[P]$	$6/mmm$		
		rank-4	
$[2,0]SV$	$\bar{3}m$	$R,\ P_S$	$R\bar{3}m(00\gamma),\ P\bar{3}1m(\frac{1}{3}\frac{1}{3}\gamma)$
$[2,0]V^2$	$6/mmm$	P	$P6/mmm(00\gamma)$
		rank-5	
$[2,0]SV^2$	$\bar{3}m$	$R,\ P_S$	$R\bar{3}m(00\gamma,00\nu),\ P\bar{3}1m(\frac{1}{3}\frac{1}{3}\gamma,00\nu)$
$[2,0]V^3$	$6/mmm$	P	$P6/mmm(00\gamma,00\nu)$
$[4,0]S$	$\bar{3}m$	$R,\ P^S$	$R\bar{3}m(\alpha 00),\ P\bar{3}1m(\alpha\alpha\frac{1}{3})$
$[4,0]V$	$6/mmm$	P	$P6/mmm(\alpha 00)$
$[2,2]S$	$\bar{3}m$	$R,\ P^S$	$R\bar{3}m(\alpha\alpha 0),\ P\bar{3}m1(\alpha 0\frac{1}{3})$
$[2,2]V$	$6/mmm$	P	$P6/mmm(\alpha\alpha 0)$
$[4]S$	$\bar{3}$	$R,\ P^S$	$R\bar{3}(\alpha\beta 0),\ P\bar{3}(\alpha\beta\frac{1}{3})$
$[4]V$	$6/m$	P	$P6/m(\alpha\beta 0)$
		rank-6	
$[2,0]SV^3$	$\bar{3}m$	$R,\ P_S$	$R\bar{3}m(00\gamma,00\nu,00\theta),\ P\bar{3}1m(\frac{1}{3}\frac{1}{3}\gamma,00\nu,00\theta)$
$[2,0]V^4$	$6/mmm$	P	$P6/mmm(00\gamma,00\nu,00\theta)$
$[4,0]S^2$	$\bar{3}m$	$R,\ P_S^S$	$R\bar{3}m(\alpha 0\gamma),\ P\bar{3}1m(\alpha\alpha\frac{1}{3},\frac{1}{3}\frac{1}{3}\gamma)$
$[4,0]SV$	$\bar{3}m$	$R,\ P_S,$ $P^S,\ P$	$R\bar{3}m(\alpha 00,00\gamma),\ P\bar{3}1m(\alpha 00,\frac{1}{3}\frac{1}{3}\gamma),$ $P\bar{3}1m(\alpha\alpha\frac{1}{3},00\gamma),\ P\bar{3}1m(\alpha\alpha\gamma)$
$[4,0]V^2$	$6/mmm$	P	$P6/mmm(\alpha 0\gamma)$
$[2,2]SV$	$\bar{3}m$	$R,\ P_S,$ $P^S,\ P$	$R\bar{3}m(\alpha\alpha 0,00\gamma),\ P\bar{3}1m(\alpha\alpha 0,\frac{1}{3}\frac{1}{3}\gamma),$ $P\bar{3}m1(\alpha 0\frac{1}{3},00\gamma),\ P\bar{3}m1(\alpha 0\gamma)$
$[2,2]V^2$	$6/mmm$	P	$P6/mmm(\alpha\alpha\gamma)$
$[4]S^2$	$\bar{3}$	$R,\ P_S^S$	$R\bar{3}(\alpha\beta\gamma),\ P\bar{3}(\alpha\beta\frac{1}{3},\frac{1}{3}\frac{1}{3}\gamma)$
$[4]SV$	$\bar{3}$	$R,\ P_S,$ $P^S,\ P$	$R\bar{3}(\alpha\beta 0,00\gamma),\ P\bar{3}(\alpha\beta 0,\frac{1}{3}\frac{1}{3}\gamma),$ $P\bar{3}(\alpha\beta\frac{1}{3},00\gamma),\ P\bar{3}(\alpha\beta\gamma)$
$[4]V^2$	$6/m$	P	$P6/m(\alpha\beta\gamma)$

Table 4.2 (Continued)

Bravais Class	**Point Group**	**(3+d) Settings**	**JJdW Symbol**
		rank-7	
$[2,0]SV^4$	$\bar{3}m$	R, P_S	$R\bar{3}m(00\gamma,00\nu,00\theta,00\mu)$, $P\bar{3}1m(\frac{1}{3}\frac{1}{3}\gamma,00\nu,00\theta,00\mu)$
$[2,0]V^5$	$6/mmm$	P	$P6/mmm(00\gamma,00\nu,00\theta,00\mu)$
$[4,0]S^2V$	$\bar{3}m$	$R,\ P_S^S,$ P_S	$R\bar{3}m(\alpha0\gamma,00\nu),\ P\bar{3}1m(\alpha0\frac{1}{3},\frac{1}{3}\frac{1}{3}\gamma,00\nu),$ $P\bar{3}1m(\alpha\alpha\gamma,\frac{1}{3}\frac{1}{3}\nu)$
$[4,0]SV^2$	$\bar{3}m$	$R,\ P_S,$ $P^S,\ P$	$R\bar{3}m(\alpha00,00\gamma,00\nu),\ P\bar{3}1m(\alpha00,\frac{1}{3}\frac{1}{3}\gamma,00\nu),$ $P\bar{3}1m(\alpha\alpha\frac{1}{3},00\gamma,00\nu),\ P\bar{3}1m(\alpha\alpha\gamma,00\nu)$
$[4,0]V^3$	$6/mmm$	P	$P6/mmm(\alpha0\gamma,00\nu)$
$[2,2]SV^2$	$\bar{3}m$	$R,\ P_S,$ $P^S,\ P$	$R\bar{3}m(\alpha\alpha0,00\gamma,00\nu),\ P\bar{3}1m(\alpha\alpha0,\frac{1}{3}\frac{1}{3}\gamma,00\nu),$ $P\bar{3}m1(\alpha0\frac{1}{3},00\gamma,00\nu),\ P\bar{3}m1(\alpha0\gamma,00\nu)$
$[2,2]V^3$	$6/mmm$	P	$P6/mmm(\alpha\alpha\gamma,00\nu)$
$[4]S^2V$	$\bar{3}$	$R,\ P_S^S,$ P_S	$R\bar{3}(\alpha\beta\gamma,00\nu),\ P\bar{3}(\alpha\beta\frac{1}{3},\frac{1}{3}\frac{1}{3}\gamma,00\nu),$ $P\bar{3}(\alpha\beta\gamma,\frac{1}{3}\frac{1}{3}\nu)$
$[4]SV^2$	$\bar{3}$	$R,\ P_S,$ $P^S,\ P$	$R\bar{3}(\alpha\beta0,00\gamma,00\nu),\ P\bar{3}(\alpha\beta0,\frac{1}{3}\frac{1}{3}\gamma,00\nu),$ $P\bar{3}(\alpha\beta\frac{1}{3},00\gamma,00\nu),\ P\bar{3}(\alpha\beta\gamma,00\nu)$
$[4]V^3$	$6/m$	P	$P6/m(\alpha\beta\gamma,00\nu)$
$[6,0]S$	$\bar{3}m$	$R,\ P^S$	$R\bar{3}m(\alpha00,\beta00),\ P\bar{3}1m(\alpha\alpha\frac{1}{3},\beta00)$
$[6,0]V$	$6/mmm$	P	$P6/mmm(\alpha00,\beta00)$
$[4,2]S$	$\bar{3}m$	$R,\ P_1^S,$ P_2^S	$R\bar{3}m(\alpha00,\beta\beta0),\ P\bar{3}1m(\alpha\alpha\frac{1}{3},\beta\beta0),$ $P\bar{3}m1(\alpha0\frac{1}{3},\beta\beta0)$
$[2,4]S$	$\bar{3}m$	$R,\ P^S$	$R\bar{3}m(\alpha\alpha0,\beta\beta0),\ P\bar{3}m1(\alpha0\frac{1}{3},\beta00)$
$[4,2]V$	$6/mmm$	$P_1,\ P_2$	$P6/mmm(\alpha00,\beta\beta0),\ P6/mmm(\alpha\alpha0,\beta\beta0)$
$[6]S$	$\bar{3}$	$R,\ P^S$	$R\bar{3}(\alpha\beta0,\delta\epsilon0),\ P\bar{3}(\alpha\beta0,\delta\epsilon\frac{1}{3})$
$[6]V$	$6/m$	P	$P6/m(\alpha\beta0,\delta\epsilon0)$

4.3 Space Groups

4.3.1 Gauge-Equivalence Classes of Phase Functions

As in the rank-4 case, we exploit the decomposability of the lattices and read the gauge-equivalence classes directly from Tables 3.3 and 3.4 of the gauge-equivalence classes in the rank-3 periodic case:

(1) As in the periodic case a gauge can be picked in which the phases at all horizontal lattice generating vectors are zero.

(2) Each staggered vector and its corresponding pair of generators in the horizontal plane form an independent rank-3 trigonal R sublattice on which the phases are determined independently of their determination at the other lattice generating vectors. Therefore the phases at each staggered stacking vector can be taken directly from Table 3.4 for the rank-3 R lattice.

(3) The phases at all the vertical stacking vectors are determined independently of any of the other phases. They can therefore be taken directly from Table 3.3 of the gauge-equivalence classes for the rank-3 hexagonal P lattice.

The resulting tabulation of gauge-equivalence classes is given in parts I of Tables 4.3–4.5. For each Bravais class one needs to consider only the point groups that are subgroups of the point group of the lattices in the class, as given in Table 4.1.

4.3.2 Identification of Gauge-Equivalence Classes Under Scale Equivalence

As in our treatment of the rank-4 case, we consider integral linear combinations of the stacking vectors with determinant ± 1 that give alternative sets of stacking vectors differing from the original set only by rescalings of their vertical components. Gauge–inequivalent phase functions that differ only by these transformations belong in the same scale-equivalence class.

We make these further identifications by building up the general transformations out of transformations of pairs of stacking vectors, using the same 2×2 matrices of determinant ± 1 used in the rank-4 case, in section 3.5. There we found that except for the point groups $6mm$ and $6/mmm$, which we consider below, only one of the two stacking vectors need have non-zero phases, the phases associated with the other being taken to zero by appropriate linear transformations. In the case of arbitrary rank, we can make the same argument, picking one stacking vector and using it sequentially to form new linear combinations of each of the others at which all the phase functions are zero.[2] As a result, for all the point groups except $6mm$

[2]The procedure we followed in the rank-4 case works in exactly the same way even when applied to two *staggered* stacking vectors, a possibility which first arises in rank-6.

Table 4.3: Gauge-equivalence classes and space groups of arbitrary finite rank in the hexagonal system, and their settings for modulated periodic crystals. The hexagonal point groups are compatible with lattices containing only vertical stacking vectors: Bravais classes of type $[i,j]V^l$ and $[i]V^l$. All point groups are compatible with Bravais classes of type $[i,j]V^l$. If the Bravais class is $[i]V^l$ one need only consider the point groups $6/m$, $\bar{6}$, and 6.

The gauge-equivalence classes are given in part I of the Table. They are specified by a set of phases: the values of a representative set of phase functions for the point group generators at the primitive generating vectors of the lattices. A gauge is used in which all phases unspecified in the table are zero. The possible non-zero phases are only at the vertical stacking vectors $\mathbf{c}^\alpha$ ($\alpha = 1 \ldots l$) and only associated with the 6-fold rotation r or the vertical mirror m. These phases are taken directly from Table 3.3 of the gauge-equivalence classes for the rank-3 hexagonal P lattice.

Part II of the Table lists the space groups of arbitrary finite rank arrived at by identifying scale-equivalent gauge-equivalence classes. Again, only non-zero phases are given. Phases characterizing a given space group are on a horizontal row, enclosed in brackets [...] when more than one phase is needed. (The absence of such brackets in part I of the table indicates that any selection of phases, one from each possible column, gives a distinct gauge-equivalence class.) In all but the last case in the right hand column, only a single stacking vector has non-zero phases. The non-zero phases describing hexagonal space groups of arbitrary rank are identical to those given in Table 3.5 for the case of rank 4, since all additional lattice generating vectors can be assigned zero phases.

Part III of the Table lists the different settings of the space groups in the modulated case, where one singles out a rank-3 sublattice of main reflections, which must be taken from one of the P settings (P_1 or P_2). We take $\mathbf{c}^1$ to be the generator of the lattice of main reflections. All other stacking vectors describe satellite peaks. The settings are separated vertically into sets that correspond to settings of the general space groups listed in the same order as those sets, in part II. All settings except for the last one in the right hand column involve non-zero phases at only two stacking vectors, which are identical to the phases that specify the settings for rank 4. The last setting appears only in lattices with rank 5 or more.

Parts II and III of the table apply to lattices with more than one stacking vector. If a lattice has only a single stacking vector then the space groups and the (3+d) settings are identical to the gauge-equivalence classes, as they are in the rank-3 case. In particular enantiomorphic pairs of space groups *are* distinct when there is only one stacking vector.

G	$\bar{6}$	$6 \quad 622$	$\bar{6}2m$ $\bar{6}m2$	$6/m$	$6mm \qquad 6/mmm$
Phases	—	$\Phi_r(\mathbf{c}^\alpha)$	$\Phi_m(\mathbf{c}^\alpha)$	$\Phi_r(\mathbf{c}^\alpha)$	$\Phi_r(\mathbf{c}^\alpha) \qquad \Phi_m(\mathbf{c}^\alpha)$
I. Gauge Equiva- lence Classes		0 $\frac{1}{6}$ $\frac{2}{6}$ $\frac{3}{6}$ $\frac{4}{6}$ $\frac{5}{6}$	0 $\frac{1}{2}$	0 $\frac{1}{2}$	$0 \qquad 0$ $\frac{1}{2} \qquad \frac{1}{2}$
Phases	—	$\Phi_r(\mathbf{c}^1)$	$\Phi_m(\mathbf{c}^1)$	$\Phi_r(\mathbf{c}^1)$	$\Phi_r(\mathbf{c}^1) \quad \Phi_m(\mathbf{c}^1) \qquad \Phi_r(\mathbf{c}^2) \quad \Phi_m(\mathbf{c}^2)$
II. General rank-n Space Groups		0 $\frac{1}{6}$ $\frac{2}{6}$ $\frac{3}{6}$	0 $\frac{1}{2}$	0 $\frac{1}{2}$	$[\ 0 \quad 0 \qquad 0 \quad 0\ ]$ $[\ \frac{1}{2} \quad 0 \qquad 0 \quad 0\ ]$ $[\ 0 \quad \frac{1}{2} \qquad 0 \quad 0\ ]$ $[\ \frac{1}{2} \quad \frac{1}{2} \qquad 0 \quad 0\ ]$ $[\ 0 \quad \frac{1}{2} \qquad \frac{1}{2} \quad 0\ ]$
Phases	—	$\Phi_r(\mathbf{c}^1)\Phi_r(\mathbf{c}^2)$	$\Phi_m(\mathbf{c}^1)\Phi_m(\mathbf{c}^2)$	$\Phi_r(\mathbf{c}^1)\Phi_r(\mathbf{c}^2)$	$\Phi_r(\mathbf{c}^1)\Phi_m(\mathbf{c}^1) \quad \Phi_r(\mathbf{c}^2)\Phi_m(\mathbf{c}^2) \quad \Phi_r(\mathbf{c}^3)\Phi_m(\mathbf{c}^3)$
III. Settings of General Space Groups for Modul- ated Crystals		$[\ 0 \quad 0\ ]$ $[\ \frac{1}{6} \quad 0\ ]$ $[\ \frac{2}{6} \quad \frac{1}{6}\ ]$ $[\ \frac{3}{6} \quad \frac{1}{6}\ ]$ $[\ \frac{4}{6} \quad \frac{1}{6}\ ]$ $[\ \frac{5}{6} \quad 0\ ]$ $[\ 0 \quad \frac{1}{6}\ ]$ $[\ \frac{2}{6} \quad 0\ ]$ $[\ \frac{4}{6} \quad 0\ ]$ $[\ 0 \quad \frac{2}{6}\ ]$ $[\ \frac{3}{6} \quad 0\ ]$ $[\ 0 \quad \frac{3}{6}\ ]$	$[\ 0 \quad 0\ ]$ $[\ \frac{1}{2} \quad 0\ ]$ $[\ 0 \quad \frac{1}{2}\ ]$	$[\ 0 \quad 0\ ]$ $[\ \frac{1}{2} \quad 0\ ]$ $[\ 0 \quad \frac{1}{2}\ ]$	$[\ 0 \quad 0 \qquad 0 \quad 0 \qquad 0 \quad 0\ ]$ $[\ \frac{1}{2} \quad 0 \qquad 0 \quad 0 \qquad 0 \quad 0\ ]$ $[\ 0 \quad 0 \qquad \frac{1}{2} \quad 0 \qquad 0 \quad 0\ ]$ $[\ 0 \quad \frac{1}{2} \qquad 0 \quad 0 \qquad 0 \quad 0\ ]$ $[\ 0 \quad 0 \qquad 0 \quad \frac{1}{2} \qquad 0 \quad 0\ ]$ $[\ \frac{1}{2} \quad \frac{1}{2} \qquad 0 \quad 0 \qquad 0 \quad 0\ ]$ $[\ 0 \quad 0 \qquad \frac{1}{2} \quad \frac{1}{2} \qquad 0 \quad 0\ ]$ $[\ 0 \quad \frac{1}{2} \qquad \frac{1}{2} \quad 0 \qquad 0 \quad 0\ ]$ $[\ \frac{1}{2} \quad 0 \qquad 0 \quad \frac{1}{2} \qquad 0 \quad 0\ ]$ $[\ \frac{1}{2} \quad \frac{1}{2} \qquad \frac{1}{2} \quad 0 \qquad 0 \quad 0\ ]$ $[\ 0 \quad 0 \qquad 0 \quad \frac{1}{2} \qquad \frac{1}{2} \quad 0\ ]$

Table 4.4: Gauge-equivalence classes and space groups of arbitrary finite rank in the trigonal system for lattices containing only vertical stacking vectors (Bravais classes of type $[i,j]V^l$ and $[i]V^l$), and their settings for modulated periodic crystals. All trigonal point groups are compatible with Bravais classes of type $[i,j]V^l$. If the Bravais class is $[i]V^l$ one need only consider the point groups $\bar{3}$ and 3. The structure and conventions are the same as for Table 4. The non-zero phases describing these space groups and their P settings (P_1 or P_2) for modulated periodic crystals are identical to those given in Table 3.6 for the case of rank-4, since all additional lattice generating vectors can be assigned zero phases.

G	$\bar{3}$	3 $\begin{matrix}321\\312\end{matrix}$	$\begin{matrix}3m1 & 3m1\\ \bar{3}1m & 31m\end{matrix}$
Phases	—	$\Phi_r(\mathbf{c}^\alpha)$	$\Phi_m(\mathbf{c}^\alpha)$
I. Gauge		0	0
Equivalence		$\frac{1}{3}$	$\frac{1}{2}$
Classes		$\frac{2}{3}$	
Phases	—	$\Phi_r(\mathbf{c}^1)$	$\Phi_m(\mathbf{c}^1)$
II. General rank-n		0	0
Space Groups		$\frac{1}{3}$	$\frac{1}{2}$
Phases	—	$\Phi_r(\mathbf{c}^1)$ $\Phi_r(\mathbf{c}^2)$	$\Phi_m(\mathbf{c}^1)$ $\Phi_m(\mathbf{c}^2)$
III. Settings of General		$[\ 0 \quad 0\ ]$	$[\ 0 \quad 0\ ]$
Space Groups			
for Modulated Crystals		$[\ \frac{1}{3} \quad 0\ ]$	$[\ \frac{1}{2} \quad 0\ ]$
		$[\ \frac{2}{3} \quad 0\ ]$	$[\ 0 \quad \frac{1}{2}\ ]$
		$[\ 0 \quad \frac{1}{3}\ ]$	

Table 4.5: Gauge-equivalence classes and space groups of arbitrary finite rank in the trigonal system for lattices containing at least one staggered stacking vector (Bravais classes of type $[i,j]S^kV^l$ and $[i]S^kV^l$ with $k > 0$), and their settings for modulated periodic crystals. All trigonal point groups are compatible with Bravais classes of type $[i,j]S^kV^l$. If the Bravais class is $[i]S^kV^l$ one need only consider the point groups $\bar{3}$ and 3.

The structure and conventions are the same as for Table 4, except that the settings of the space groups for modulated crystals occupy Parts III-V, corresponding to the three types of settings for the Bravais classes P, R, and P^S. (The entries for P apply equally well to the P_1, P_2, and P_S, settings, and those for P^S apply equally well to P_1^S, P_2^S, and P_S^S.)

The phases in Part I for the gauge-equivalence classes are identical to those in Table 3.4 of the gauge-equivalence classes for the rank-3 trigonal R lattice.

When the point group is 3 or 32 and the lattice has no vertical stacking vectors, there are only symmorphic space groups (*i.e.* all phases can be taken to be zero). The table entries only apply when there is at least one vertical stacking vector.

When the point group is $\bar{3}m$ or $3m$, $\Phi_m(\mathbf{c}')$ denotes the non-zero phase associated with a stacking vector that can be taken to be either vertical or staggered if both possibilities are available. The simplest convention is to take it to be vertical whenever possible.

We take the generator of the lattice of main reflections to be $\mathbf{c}^1$ for the P settings, $\mathbf{c}_s^1$ for the R settings, and $\mathbf{c} = 3\mathbf{c}_s^1 - 2\mathbf{a} - \mathbf{b}$ for the P^S settings, where $\mathbf{a}$ and $\mathbf{b}$ are the horizontal generating vectors associated with $\mathbf{c}_s^1$. In the P^S settings the phase of the stacking vector for the lattice of main reflections is also assigned to two satellite stacking vectors, $\mathbf{c}_s^1$ and $(\mathbf{c}_s^1 - \mathbf{a})$, as noted in section 4.4.2. The P^S settings are possible only in ranks greater than 4.

G	$\bar{3}$	3 32	$\bar{3}m$ $3m$
Phases	—	$\Phi_r(\mathbf{c}^\alpha)$	$\Phi_m(\mathbf{c}_s^\beta)$ $\Phi_m(\mathbf{c}^\alpha)$
I. Gauge		0	0 0
Equivalence		$\frac{1}{3}$	$\frac{1}{2}$ $\frac{1}{2}$
Classes		$\frac{2}{3}$	
Phases	—	$\Phi_r(\mathbf{c}^1)$	$\Phi_m(\mathbf{c}')$
II. General rank-n		0	0
Space Groups		$\frac{1}{3}$	$\frac{1}{2}$
Phases	—	$\Phi_r(\mathbf{c}^1)$	$\Phi_m(\mathbf{c}^1)$ $\Phi_m(\mathbf{c}')$
III. P Settings of General		0	[0 0]
Space Groups			
for Modulated Crystals		$\frac{1}{3}$	[$\frac{1}{2}$ 0]
		$\frac{2}{3}$	[0 $\frac{1}{2}$]
Phases	—	$\Phi_r(\mathbf{c}^1)$	$\Phi_m(\mathbf{c}_s^1)$ $\Phi_m(\mathbf{c}')$
IV. R Settings of General		0	[0 0]
Space Groups			
for Modulated Crystals		$\frac{1}{3}$	[$\frac{1}{2}$ 0]
			[0 $\frac{1}{2}$]
Phases	—	$\Phi_r(\mathbf{c}^1)$	$\Phi_m(\mathbf{c})$ $\Phi_m(\mathbf{c}')$
V. P^S Settings of General		0	[0 0]
Space Groups			
for Modulated Crystals		$\frac{1}{3}$	[$\frac{1}{2}$ 0]
			[0 $\frac{1}{2}$]

and $6/mmm$, the space groups for any number of stacking vectors are exactly the same as in the rank-4 case: the non-zero phases can be associated with a single stacking vector. Unless all stacking vectors are staggered that single vector can be taken to be vertical, and the phases are exactly as for the rank-3 periodic P lattice (Table 3.3), except for the simplifying identification of enantiomorphic pairs that exists when the rank exceeds 3. If all stacking vectors are staggered then the phases at the stacking vector with non-zero phase are exactly as for the rank-3 periodic R lattice (Table 3.4). This is shown in parts II of Tables 4.3–4.5.

It remains to consider the point groups $6mm$ and $6/mmm$. These allow only vertical stacking vectors, and allow non-zero values for both Φ_r and Φ_m. There are only three choices for the possible non-zero pairs of phases $[\Phi_r, \Phi_m]$ at each stacking vector: $[0\ \frac{1}{2}]$, $[\frac{1}{2}\ 0]$, and $[\frac{1}{2}\ \frac{1}{2}]$. We can therefore reduce the maximum number of vectors with non-zero phases to three, by selecting one with each of the three types of phases and simply adding it to any other vector of that type.[3] If stacking vectors with all three types of phases are present, we can also reduce both phases at one of the remaining three to zero, by adding to it the sum of the other two. To group the gauge-equivalence classes into space groups, we need therefore consider only a pair of vertical stacking vectors with non-zero phases, just as in the rank-4 case. Therefore for the remaining point groups, $6mm$ and $6/mmm$, the space groups for any number of stacking vectors are also exactly the same as in the rank-4 case. The non-zero phases can be associated with a pair of vertical stacking vectors, and are given in the column on the right of part II of Table 4.3.

4.4 Settings for the $(3 + d)$ Modulated Case

We stress that in contrast to the rank-4 case, the $(3 + d)$ settings are just one example of the settings in which one can display the general space groups, useful in the case when the modulated structure is a periodic crystal. More general $(m + d)$ settings would be useful if one wished to describe weak modulations of a general quasiperiodic crystal of rank m. We focus here on the $(3 + d)$ settings because these are currently the ones of practical importance, and because this enables us to establish the relation of our own approach to that of JJdW[1], who have enumerated, using the superspace approach, the settings of the Bravais classes for $d = 1, 2, 3$, denoting them as "(3+d) Bravais classes". The associated "superspace groups for modulated crystals"—the (3+d) settings of the space groups—have only been given for the (3+1) case (see de Wolff, Janssen, and Janner[3], and Janssen *et. al*[2].

Table 4.6: The (3+d) settings of the hexagonal and trigonal Bravais classes $[i,j]S^kV^l$ of rank $i+j+k+l = 3+d$. The settings for lattices of type $[i]S^kV^l$ are the same as those for lattices of type $[i,0]S^kV^l$. The subscripts 1 and 2 can be omitted when a Bravais class only admits one of the two settings they distinguish. For a Bravais class to have all seven settings we require $k \geq 2$, $i \geq 6$, $j \geq 2$, and $l \geq 1$, so the one of least rank with all seven is the Bravais class $[6,2]S^2V$ of rank-11.

Settings	**Conditions on** $[i,j]S^kV^l$
P_1	$l > 0, \quad i > 2k$
P_2	$l > 0, \quad j > 0, \quad i \neq j$ if $k = 0$
P_S	$l > 0, \quad k > 0$
P_1^S	$k > 0, \quad i > 2k$
P_2^S	$k > 0, \quad j > 0$
P_S^S	$k > 1$
R	$k > 0$

4.4.1 Settings of the General Bravais Classes

A rank-3 sublattice, serving as a lattice of main reflections, is itself either a trigonal or a hexagonal (periodic) lattice, and as such must include one star of horizontal generating vectors and a single stacking vector. There are three distinct possibilities for the stacking vector of main reflections:

(1) it can be a vertical stacking vector from the full lattice;

(2) it can be three times the vertical part of a staggered stacking vector of the full lattice;

(3) it can be a staggered stacking vector of the full lattice.

Cases (1) and (2) have P lattices of main reflections and case (3) has R lattices. We distinguish the settings of type (1) and (2) by calling them P settings and P^S settings respectively.

In specifying for any given Bravais class which of the P, P^S, and R settings can be realized and in how many distinct ways, it is enough to consider Bravais classes of type $[i,j]$, since the settings of a Bravais class of type $[\,i\,]$ are identical to those of type $[i,0]$. Whether the stars are all aligned (type $[i,0]$) or not aligned at all (type $[\,i\,]$) is irrelevant to the settings, since in either case the only grounds for

[3]The result is zero because phase arithmetic is modulo unity.

distinguishing among stars is whether or not they are associated with a staggered vector.

Case (1): P settings. When the stacking vector of main reflections is a vertical stacking vector of the full lattice there can be up to three distinct choices for the star of main reflections. If the star is associated with a staggered stacking vector we have a P_S setting. If it is not, then there can in general be two additional settings, depending on which set of stars the star of main reflections is taken from. We denote the two settings by P_1 and P_2 depending on whether the star of main reflections is taken from the set specified by i or j in the $[i, j]$ symbol. When only one possibility is available (*i.e.* when $j = 0$, or when $i = j$ and there are no staggered stacking vectors) the subscript may be omitted.

Case (2): P^S settings. When the stacking vector of main reflections is 3 times the vertical part of a staggered stacking vector $\mathbf{c_s}$ of the full lattice, the star of main reflections can be from any horizontal star of the full lattice except the one associated with $\mathbf{c_s}$. If the full lattice has a second staggered stacking vector $\mathbf{c_s}'$, then its associated star gives a setting we call P^S_S. If the star of main reflections is not associated with another staggered stacking vector, then as in case (1) there are in general two settings, P^S_1 and P^S_2, which may be denoted simply by P^S when only one possibility is available.

Case (3): R settings. The lattice of main reflections can be an R lattice whenever the full lattice contains at least one staggered stacking vector. The star of main reflections must then be the one uniquely associated with that staggered vector, and there is just one such setting.

The settings are summarized in full generality in Table 4.6, and are listed in the third column of Table 4.2 for all Bravais classes from rank 4 to rank 7.

4.4.2 Settings of the General Space Groups

Case (1): All point groups except $6mm$ and $6/mmm$.

These point groups assign non-zero phases to only a single point group generator.

Case (1A): R and P settings. If the Bravais class of the main reflections is given by the R, P_1, P_2, or P_S setting of the general Bravais class, then the stacking vector for the main reflections, whose phases must not be altered by the transformations that establish scale equivalence, is one of the vertical or staggered generating vectors of the full lattice. Since the transformations that act only on the satellite stacking vectors are entirely unrestricted, the analysis of the phase functions associated with the satellite stacking vectors is identical to our analysis of *unrestricted* scale-equivalence that led to the general space groups. In that case we found that all but a single stacking vector could be given zero phases. The analysis of the *restricted* scale equivalence for that single satellite stacking vector and the stacking vector for the main reflections is then identical to the analysis we performed in the rank-4

case, leading directly to the settings given in parts III of Tables 4.3 and 4.4 and in parts III and IV of Table 4.5.

Case (1B): P^S settings. If the Bravais class of main reflections is given by the settings P_1^S, P_2^S, or P_S^S—possibilities that do not arise in the rank-4 case— then the stacking vector for the main reflections is three times the vertical component of one of the staggered stacking vectors $\mathbf{c_s}$ for the full lattice. If $\mathbf{a}$ and $\mathbf{b}$ are the horizontal generating vectors associated with $\mathbf{c_s}$, then the stacking vector for the main reflections is

$$\mathbf{c} = 3\mathbf{c_s} - 2\mathbf{a} - \mathbf{b} \tag{4.2}$$

and among the generating vectors for the satellites there are two with non-zero horizontal components that can be taken to be

$$\mathbf{s}_1 = \mathbf{c_s}, \quad \mathbf{s}_2 = \mathbf{c_s} - \mathbf{a} \ . \tag{4.3}$$

Since the only non-zero phase $\mathbf{c_s}$ can have[4] is $\Phi_m(\mathbf{c_s}) \equiv \frac{1}{2}$ and since all phase functions vanish in the horizontal plane, the possible phases of the stacking vector for the main reflections and these two generating vectors for the satellites are not independent:

$$\Phi_m(\mathbf{c}) \equiv \Phi_m(\mathbf{s}_1) \equiv \Phi_m(\mathbf{s}_2) \equiv 0 \text{ or } \tfrac{1}{2}. \tag{4.4}$$

Note that in this case the phases available to $\mathbf{c}$, the generating vector for a P lattice of main reflections, must be taken from the set of phases appropriate to the rank-3 R lattice.

Having noted that $\Phi_m(\mathbf{c})$ is restricted by (4.4) and that its value entirely determines the phases at the satellite generating vectors $\mathbf{s}_1$ and $\mathbf{s}_2$, we can proceed with the remaining satellite stacking vectors just as we did for the other four settings, concluding that all but one of the remaining satellite stacking vectors can be assigned zero phases.

When the point groups are 3 and 32 there are no non-vanishing mirror phase functions and the above complication does not arise. In this case the settings of the space groups are exactly as given for the R settings: a non-zero phase can be associated with a single vertical satellite stacking vector, if one exists.

When the point groups are $\bar{3}m$ or $3m$ then in addition to the two possible values of the phases in (4.4) we need to consider the possible values of 0 or $\frac{1}{2}$ for the phase of a single additional stacking vector for the satellites, whether it is staggered or vertical.[5] These four possibilities yield only three settings, the one with both phases $\frac{1}{2}$ being scale-equivalent to the one where the phases in (4.4) are $\frac{1}{2}$ and the phase of the additional stacking vector is 0.

The P^S settings of the space groups are summarized in part V of Table 4.5.

[4]See part I of Table 4.5.

[5]It would be simplest to choose it to be a vertical vector if one is available.

Case (2): Point groups $6mm$ *and* $6/mmm$ *(Only P settings are possible).*

When the point group is $6mm$ or $6/mmm$ all stacking vectors are vertical so the complications of the P^S settings do not arise, but now both Φ_r and Φ_m can be non-zero. Evidently if there are just two stacking vectors the settings are exactly as in the rank-4 case. When there are 3 or more, let $\mathbf{c}^1$ be the one that indexes the main reflections. Scale-equivalence transformations that act only on the remaining stacking vectors are entirely unrestricted, and therefore the analysis of the scale-equivalence classes of phase functions associated with the remaining stacking vectors is identical to our analysis of *unrestricted* scale-equivalence, which led to the phases that characterize the general space groups. Thus we can index the satellites in such a way that at most two of the satellite stacking vectors $\mathbf{c}^2$ and $\mathbf{c}^3$ have non-zero phases, and the possible choices for those phases are the same five sets that part II of Table 4.3 assigns to $\mathbf{c}^1$ and $\mathbf{c}^2$ in the general space groups.

In four of those five sets one of the two stacking vectors $\mathbf{c}^2$ and $\mathbf{c}^3$ is assigned zero phases. If we take that one to be $\mathbf{c}^3$, then in determining restricted scale-equivalence, we need only examine restricted scale-equivalence transformations that act on the stacking vector of main reflections $\mathbf{c}^1$ and the satellite stacking vector $\mathbf{c}^2$. But this is exactly the procedure we followed in Chapter 3 to determine the settings for modulated crystals in the rank-4 case, where we found the ten settings listed in Table 3.5. These same sets of phases, with phases 0 assigned to $\mathbf{c}^3$, form the first ten entries in the right hand column of Part III of Table 4.3.

The eleventh entry arises from the fifth possible assignment of phases to the satellite stacking vectors $\mathbf{c}^2$ and $\mathbf{c}^3$, in which $[\Phi_r, \Phi_m]$ has the value $[0, \frac{1}{2}]$ at $\mathbf{c}^2$ and $[\frac{1}{2}, 0]$ at $\mathbf{c}^3$. The accompanying phases at the stacking vector of main reflections $\mathbf{c}^1$ can independently have the full set of values $[0, 0]$, $[0, \frac{1}{2}]$, $[\frac{1}{2}, 0]$, or $[\frac{1}{2}, \frac{1}{2}]$. The restricted scale-equivalence transformations allow us to add $\mathbf{c}^1$ to either of the satellite stacking vectors $\mathbf{c}^2$ or $\mathbf{c}^3$, and to add one of $\mathbf{c}^2$ or $\mathbf{c}^3$ to the other. As a result except when $\mathbf{c}^1$ has both phases 0, we can again reduce the phase associated with one of the two satellite stacking vectors to zero, thereby establishing scale equivalence with one of the ten cases already listed. For each point group there is thus only one additional setting beyond the ten we found in the rank-4 case. This is a setting of the fifth space group in part II of Table 4.3. The setting has non-zero phases only at the two stacking vectors $\mathbf{c}^2$ and $\mathbf{c}^3$, and is listed as the last entry in part III of Table 4.3.

Bibliography

[1] A. Janner, T. Janssen, and P. M. de Wolff, "Bravais classes for incommensurate crystal phases", *Acta Cryst.* A**39** (1983) 658-666.

[2] T. Janssen, A. Janner, A. Looijenga-Vos, and P. M. de Wolff, "Incommensurate and commensurate modulated structures", *International Tables for Crystallography, Volume C,* Ed. A. J. C. Wilson (Kluwer Academic, Dodrecht, 1992) 797-844.

[3] P. M. de Wolff, T. Janssen, and A. Janner, "The superspace groups for incommensurate crystal structures with a one-dimensional modulation", *Acta Cryst.* A**37** (1981) 625-636.

Chapter 5

Concluding Remarks

5.1 The Main Result

Our purpose has been to demonstrate the applicability of Fourier-space crystallography to the symmetry classification of incommensurately modulated crystals and composite crystals. This has been established through the enumeration of all the Bravais classes for the simplest reducible incommensurate lattices (all 3-dimensional rank-4 Bravais classes and all 3-dimensional rank-6 cubic and tetrahedral Bravais classes), and the enumeration of all Bravais classes and space groups for hexagonal and trigonal crystals of arbitrary finite rank. For each of these Bravais classes and space groups we found the different settings which emphasize the existence of a rank-3 sublattice of main reflections, independently invariant under the point group of the crystal.

If no distinctions are made between strong and weak reflections in the diffraction pattern of a crystal then its symmetry is described by its space group without regard to setting. This is the case for *periodic crystals* and *quasicrystals*.

If the structure is a *modulated crystal*, characterized by the existence of a single sublattice of main reflections, then we supplement the specification of the space group by stating which of the possible sublattices of the full lattice contains the strong peaks. Identifying a particular sublattice of main reflections can be viewed as using a particular setting of the space group which emphasizes the existence of that sublattice. This is done by choosing a set of generating vectors for the full lattice of which the first three generate just the lattice of main reflections. Thus the symmetry of the crystal is again described by its space group, given in the appropriate setting.

If the structure is a *composite crystal* with two or more sublattices of main reflections then we supplement the space group description by specifying *all* of the sublattices that contain main reflections, *i.e.* by listing all the appropriate settings. The same procedure applies to the case of *modulated quasicrystals* or hypothetical *composite quasicrystals* with the only difference that one is looking for sublattices

of main reflections whose rank is greater than 3 (and of course less than the rank of the full lattice).

The superspace approach lacks this flexibility in dealing with different types of crystals. It was specifically designed to deal with incommensurately modulated periodic crystals and therefore always requires the existence of a single rank-3 sublattice of main reflections. Problems arise when one tries to describe structures with no main reflections as in quasicrystals or structures with multiple sublattices of main reflections as in composite crystals. When applying the superspace approach to composite crystals one is led to the redundant description of a single crystal by a number of *different* superspace groups. It is not always evident whether two given superspace groups can serve as different descriptions of the same composite crystal.[1] This problem is avoided in the Fourier-space description which uses a single space group. Information regarding the possible sublattices of main reflection is given by the settings of this space group which are easily determined.

5.2 Technical Aspects

On the practical side of enumeration we have introduced a number of general techniques which should be useful in the future. These all rely heavily on the 3-dimensional nature of the Fourier-space approach and on our ability to apply familiar geometric intuition in 3-dimensional space. We pedagogically introduced the modular lattice method for the enumeration of Bravais classes. It was previously used by Rokhsar, Mermin, and Wright[5] as part of the enumeration of the rank-6 icosahedral Bravais classes, and it was used in Chapter 2 for the enumeration of all the Bravais classes for the simplest reducible incommensurate lattices. Its significance is in reducing the Bravais class counting to a finite procedure by having to consider only a finite number of modular lattices.

We have made substantial use of the 3-dimensional nature of the Fourier-space approach in enumerating, for a given set of point groups — the hexagonal and trigonal ones — all Bravais classes of arbitrary finite rank. Once it was established (in Appendix A) that all such lattices are decomposable into only three types of small building blocks, the enumeration was reduced to a simple consideration of the distinct ways of putting these building blocks together. The enumeration in Chapter 4 only required us to consider the distinct ways of putting together the different building blocks. A more general question to which we still do not have an answer is how to determine the set of indecomposable Bravais classes for any given point group. We have shown that all 3-dimensional rank-4 lattices are decomposable. Is this an indication also for the orthorhombic system, for example, that all

[1] In fact, van Smaalen[6] gives the symmetry of $(LaS)_{1.14}NbS_2$ using the symbols of two JJdW superspace groups $Fm2m(\alpha,0,0)00s$ and $Cm2a(\alpha^{-1},0,1/2)$ which cannot describe the same rank-4 structure, as seen by a quick glance at Table 2.1. See Lifshitz and Mermin[3] for the Fourier-space description of the same composite crystal.

the indecomposable lattices are present already in rank-3, or can we expect to find another indecomposable orthorhombic lattice at some rank greater than 4? This question is equivalent to finding all the indecomposable integral representations of a given group, for which, as far as we know, no simple character formula exists (as in the cases of complex or real representations).

In enumerating space groups we emphasized in Chapter 3 the importance of specifying the lattices in a decomposable form. We showed that whenever this is possible the computation of the gauge-equivalence classes is entirely routine. One simply considers the different possibilities, already calculated for the lower-rank constituent sublattices. Thus only the three rank-6 tetrahedral Bravais classes, of all the lattices enumerated in Chapter 2 require significant additional computation and even in this case their simple relation in Fourier space to the rank-6 icosahedral quasicrystals, whose space groups have already been classified, offers important insight.[2] The decomposition principle also enabled us in Chapter 4 to easily extend our space-group classification of hexagonal and trigonal crystals to arbitrary finite rank, thus demonstrating the power and simplicity of the Fourier-space approach.

Finally, we would again like to emphasize the generality of our approach. By first focusing only on the gauge-equivalence classes of phase functions, we give the results of the non-trivial part of the calculation in a form that applies to arbitrary quasiperiodic crystals of the appropriate symmetry and rank. By deferring to the end the bookkeeping question of which classes to further identify through scale-equivalence we retain the freedom to use whatever transformations are appropriate to the material of interest. In such a way we recover both the space groups and their settings which may be used to emphasize particular sublattices of main reflections, making straightforward the treatment of materials even when they fail to fit neatly into any particular conventional category (modulated crystals, composite crystals, and quasicrystals) and allowing for a unified description of materials that might interpolate between the different categories.

5.3 Which Convention Should One Follow?

We have seen that it is useful and important to note the various ways of describing each of our rank-D Bravais classes in terms of rank-3 sublattices of main reflections and satellite peaks. We emphasize again that these are merely alternative descriptions of one and the same class of lattices of wave vectors. It is a matter of convention whether one choses (as JJdW do) to label these different representations of identical classes of lattices as distinct Bravais classes, or to regard them (as we do) as different descriptions of a single Bravais class.

In support of our convention, we would argue that using the term "Bravais class"

[2]For the enumeration of the rank-6 tetrahedral space groups and their relation to the icosahedral space groups see Dräger, Lifshitz, and Mermin[1,2].

in a way that requires one to specify the intensities as well as the positions of the Bragg peaks introduces a degree of imprecision into a set of categories that would otherwise be rigorously based on symmetry alone. With such a convention one must ask how much more intense the main reflections must be than the satellite peaks, before the scheme breaks down. Such a convention also requires independent treatments in the case of quasiperiodic crystals which fail to reveal a pronounced lattice of main reflections and in the case of composite crystals which reveal more than one such lattice.

Furthermore, if one fails to recognize the redundancy of the JJdW scheme of Bravais classes, when one computes the space groups associated with each Bravais class one is led to unnecessary additional calculations and a further redundancy of description. This redundancy also appears in any other calculation for which the outcome is independent of the choice of a sublattice of main reflections. As an example, consider the question of determining the possible low-rank space groups that may arise from a given high-rank space group through a continuous rank-lowering deformation of the lattice, as in the case of incommensurate to commensurate phase transitions observed in modulated crystals.[3] Such a calculation depends only on the positions of the wave vectors in the original lattice and not on the relative intensities of the corresponding Bragg peaks. The result should therefore be the same independent of which setting (or JJdW Bravais class) one uses for the original lattice.

[3]See Lifshitz and Mermin[4] for an example of such a calculation in Fourier-space.

Bibliography

[1] J. Dräger, R. Lifshitz, and N. D. Mermin, "Tetrahedral Quasicrystals". To appear in the proceedings of the 5th International Conference on Quasicrystals, Avignon, France, May 22-26, 1995.

[2] J. Dräger, R. Lifshitz, and N. D. Mermin. To be submitted to *Acta Cryst.* A.

[3] R. Lifshitz and N. D. Mermin, "The Symmetry of Composite Crystals". To appear in *Aperiodic '94, An International Conference on Aperiodic Crystals,* Ed. G. Chapuis (World Scientific, Singapore, 1995).

[4] R. Lifshitz and N. D. Mermin, "Symmetry Changes in Rank-Lowering Phase Transitions". To appear in *Aperiodic '94, An International Conference on Aperiodic Crystals,* Ed. G. Chapuis (World Scientific, Singapore, 1995).

[5] D. S. Rokhsar, N. D. Mermin, and D. C. Wright, "Rudimentary crystallography: The icosahedral and decagonal reciprocal lattices", *Phys. Rev* **B35** (1987) 5487–5495.

[6] S. van Smaalen, "Superspace-group approach to the modulated structure of the inorganic misfit layer compound $(LaS)_{1.14}NbS_2$", *J.Phys.:Condens. Matter* **3** (1991) 1247–1263.

Appendix A

Bravais Classes of Trigonal and Hexagonal Lattices of Arbitrary Finite Rank

We justify here the assertions made in section 4.2 about the Bravais classes of finite rank lattices with hexagonal or trigonal symmetry. When a lattice L in 3-dimensions has axial symmetry it is conveniently characterized in terms of its 2-dimensional sublattice H perpendicular to the n-fold axis, and a *modular lattice* L/H consisting of all the vectors of L taken modulo H — i.e. identified if they differ only by a vector in H. The notation reflects the fact that if L is considered as an abelian group under addition, then L/H is just the quotient group modulo the subgroup H. Since addition in L/H is just addition in L modulo vectors in H, the rank of L/H is the largest number of vectors of L that are integrally independent modulo H in a set that (modulo H) generates L/H. We refer to such a set of vectors as *stacking vectors* since the full lattice L can be viewed as a set of lattice planes given by shifting H by all integral linear combinations of the stacking vectors.

The rank D of L is just the sum of the ranks D_1 and D_2 of H and L/H:
(1) Since D_2 vectors of L can generate any vector of L to within an additive vector of H, it takes at most $D_2 + D_1$ vectors to generate every vector of L.
(2) To see that D is not less than D_1+D_2, take D_1 integrally-independent generators of H and D_2 vectors of L that taken modulo H generate L/H. If the rank of L were less than $D_1 + D_2$ then a non-trivial linear combination of these $D_1 + D_2$ vectors would vanish. Since the D_1 vectors that generate H are integrally independent, some of the coefficients of the D_2 vectors associated with L/H would have to be non-zero. But this would make an integral linear combination of these D_2 vectors equal to a vector in H, contradicting the fact that they are integrally independent modulo H.

Viewed as a 2-dimensional lattice, the sublattice H can have the 2-dimensional point group $6mm$ or 6. In section A.1 we derive the Bravais classes of 2-dimensional lattices of finite rank with point group $6mm$, and in section A.2, the Bravais classes

when the point group is 6. In section A.3 we derive the ways in which these 2-dimensional sublattices can be stacked to give the full 3-dimensional lattice.

A.1 Two-Dimensional Lattices with Point Group 6*mm*

We first categorize a general 2-dimensional lattice H of finite rank with $6mm$ symmetry in terms of a family of stars all with the same orientation by envoking again the "modular lattice method", introduced in section 2.3.1. We then note that this description is equivalent to the $[i, j]$ Bravais classes described in section 4.2, based on families of stars with two distinct orientations.

A.1.1 A description with a single family of stars

Let $\hat{\mathbf{a}}$ and $\hat{\mathbf{b}}$ be unit vectors, 120 degrees apart, on invariant lines of two vertical mirrors m_a and m_b. Expand a vector $\mathbf{v}$ in the lattice H as

$$\mathbf{v} = \alpha\hat{\mathbf{a}} + \beta\hat{\mathbf{b}} \tag{A.1}$$

(with coefficients α and β that are not necessarily rational). Twice the projections of $\mathbf{v}$ onto $\hat{\mathbf{a}}$ and $\hat{\mathbf{b}}$ must also be in H since they can be expressed as

$$\begin{array}{rcccl} 2P_a\mathbf{v} & = & \mathbf{v} + m_a\mathbf{v} & = & (2\alpha - \beta)\hat{\mathbf{a}}, \\ 2P_b\mathbf{v} & = & \mathbf{v} + m_b\mathbf{v} & = & (2\beta - \alpha)\hat{\mathbf{b}}. \end{array} \tag{A.2}$$

The subset H_a of H consisting of $2P_a\mathbf{v}$ for all $\mathbf{v}$ in H is a 1-dimensional lattice of finite rank k (since the full lattice is of finite rank) and can therefore be primitively indexed by k of its vectors; *i.e.* one can choose k integrally independent lengths $\alpha^{(1)}, \ldots, \alpha^{(k)}$ so that H_a consists of all integral linear combinations of the vectors $\mathbf{a}_1 = \alpha^{(1)}\hat{\mathbf{a}}, \ldots, \mathbf{a}_k = \alpha^{(k)}\hat{\mathbf{a}}$. By symmetry, H_b can be primitively generated by the vectors $\mathbf{b}_1 = \alpha^{(1)}\hat{\mathbf{b}}, \ldots, \mathbf{b}_k = \alpha^{(k)}\hat{\mathbf{b}}$. Note that 2-dimensional lattices of rank $2k$ that differ only in the mutually incommensurate lengths $\alpha^{(1)}, \ldots, \alpha^{(k)}$ that characterize the primitive bases for the sublattices H_a and H_b are in the same Bravais class (for essentially the same reasons that two orthorhombic P-lattices with different lattice constants (a, b and c) belong to the same Bravais class.)

We can expand the vectors (A.2) in these bases for the 1-dimensional sublattices:

$$\begin{array}{rcccl} (2\alpha - \beta)\hat{\mathbf{a}} & = & \sum_{i=1}^{k} n_i\mathbf{a}_i & = & \left(\sum_{i=1}^{k} n_i\alpha^{(i)}\right)\hat{\mathbf{a}}, \\ (2\beta - \alpha)\hat{\mathbf{b}} & = & \sum_{i=1}^{k} m_i\mathbf{b}_i & = & \left(\sum_{i=1}^{k} m_i\alpha^{(i)}\right)\hat{\mathbf{b}}. \end{array} \tag{A.3}$$

Solving for α and β enables us to express the original arbitrary vector $\mathbf{v}$ in H as

$$\mathbf{v} = \sum_{i=1}^{k} \{(\tfrac{2}{3}n_i + \tfrac{1}{3}m_i)\mathbf{a}_i + (\tfrac{1}{3}n_i + \tfrac{2}{3}m_i)\mathbf{b}_i\} \ , \tag{A.4}$$

where all the n_i and m_i are integers.

All vectors with integral coefficients for the $\mathbf{a}_i$'s and the $\mathbf{b}_i$'s are in H since they are sums of vectors in H_a and H_b. From (A.4) we learn that the lattice may also contain vectors whose coefficients are multiples of $\frac{1}{3}$ as long as the sum of the coefficients of $\mathbf{a}_i$ and $\mathbf{b}_i$ for each i is an integer. It is convenient to restate this conclusion in the form it assumes when the axes are rescaled by a factor of 3:

Any 2-dimensional hexagonal lattice of rank-$2k$ and point group $6mm$ can be expressed as a set of integral linear combination of k integrally independent parallel vectors, $\mathbf{a}_1, \ldots, \mathbf{a}_k$, and their images under a 120 degree rotation, $\mathbf{b}_1, \ldots, \mathbf{b}_k$, where: *(1)* For each i the sum of the coefficients of $\mathbf{a}_i$ and $\mathbf{b}_i$ is a multiple of 3; and *(2)* Vectors with all coefficients multiples of 3 are in the lattice and constitute a sublattice, H_P.

The 2-dimensional hexagonal lattices with point group $6mm$ can therefore be viewed as the translations through all vectors of the sublattice H_P of a finite set of vectors H_0, which can contain only vectors whose coefficients for each pair of generators $\mathbf{a}_i$ and $\mathbf{b}_i$ are 00, $1\bar{1}$, or $\bar{1}1$.[1] H_0 is the modular lattice H/H_P; it is closed under addition and subtraction modulo the lattice H_P (*i.e.* when arithmetic is performed on its components modulo 3) as a consequence of the closure of the full lattice under ordinary addition and subtraction. Since all sublattices H_P of the same rank are in the same 2-dimensional Bravais class, classifying these 2-dimensional lattices into Bravais classes reduces to classifying the corresponding modular lattices.

A.1.2 Proof by induction that all Bravais classes of 2-dimensional hexagonal lattices with $6mm$ symmetry are of type $[i, j]$

Note first the elementary geometrical fact that a pair of star vectors with a 3-element modular lattice (00, $1\bar{1}$, and $\bar{1}1$) generate exactly the same rank-2 lattice as a pair of star vectors rotated through 30 degrees and scaled down by $\sqrt{3}$, with a modular lattice containing only 00. As a result, to establish the validity of the description in section 4.2 of the horizontal sublattice in terms of two families of star-vectors at 30 degrees, we need only show that a basis of identically oriented star-generating vectors can be chosen for H_P, in terms of which the modular lattice H_0 reduces to a sum of modular lattices (each consisting either of 00 alone or the three vectors 00, $1\bar{1}$, and $\bar{1}1$) associated with each pair $\mathbf{a}_m, \mathbf{b}_m$.

This is trivially the case when the rank is 2, since there is then only one pair $\mathbf{a}, \mathbf{b}$. Suppose it has been established for rank $2k$. Then with a modular lattice H_0 of rank $2(k+1)$ it is possible to chose the first k pairs $\mathbf{a}_m, \mathbf{b}_m$ so that the sublattice of H_0 spanned by them is of type $[i, j]$ (*i.e.* H_0 is the sum of j 3–element modular lattices). If the $(k+1)$th pair $\mathbf{a}_{k+1}, \mathbf{b}_{k+1}$ does not appear in the expansion of any vector of H_0, then H_0 is of type $[i+2, j]$. Otherwise there must be at least one

[1] It is convenient to write $\bar{1}$ for -1.

vector in H_0 of the form $\mathbf{u} + \mathbf{a}_{k+1} - \mathbf{b}_{k+1}$ where $\mathbf{u}$ is a vector spanned only by the first k pairs of generating vectors. It follows that H_0 must be the sum of a modular lattice of type $[i, j]$ with a three element modular lattice that can be taken to be $[0, \mathbf{u} + \mathbf{a}_{k+1} - \mathbf{b}_{k+1}, -\mathbf{u} - \mathbf{a}_{k+1} + \mathbf{b}_{k+1}]$. If $\mathbf{u}$ is zero then H_0 is of type $[i, j+2]$. If $\mathbf{u}$ is not zero, then define

$$\mathbf{a}'_{k+1} = \mathbf{a}_{k+1} + \tfrac{2}{3} P_a \mathbf{u} \ , \quad \mathbf{b}'_{k+1} = \mathbf{b}_{k+1} - \tfrac{2}{3} P_b \mathbf{u} \ . \tag{A.5}$$

Because $\mathbf{u}$ has components 0, $1\bar{1}$, or $\bar{1}1$ along each of the first k pairs of star vectors, $-P_b\mathbf{u}$ is simply a 120 rotation of $P_a\mathbf{u}$, and $\mathbf{a}'_{k+1}$ and $\mathbf{b}'_{k+1}$ are an alternative pair of primitive star vectors for H. Since $\frac{2}{3}(P_a\mathbf{u}+P_b\mathbf{u}) = \mathbf{u}$, the 3–element modular lattice becomes $[0, \mathbf{a}'_{k+1} - \mathbf{b}'_{k+1}, -\mathbf{a}'_{k+1} + \mathbf{b}'_{k+1}]$ and H_0 is again of type $[i, j+2]$.

A.2 Two-Dimensional Lattices with Point Group 6

If the 2-dimensional point group is only 6, we must show that the lattice can be primitively generated by pairs of vectors of equal length, separated by 120 degrees. Such a lattice of finite rank i belongs to the Bravais class $[i]$ described in section 4.2.

Let $\mathbf{a}'$ be a vector vector in H and let $\mathbf{b}' = r\mathbf{a}'$ be its image under a 120 degree rotation r. Consider the sublattice H_2 of H consisting of all points which are *rational* linear combinations of $\mathbf{a}'$ and $\mathbf{b}'$. Because H has finite rank, so does H_2, which can therefore be generated by a finite number of its vectors. Because all such generating vectors are rational linear combinations of $\mathbf{a}'$ and $\mathbf{b}'$ and because they are finite in number, they can all be expressed as integral linear combinations of two rational linear combinations of $\mathbf{a}'$ and $\mathbf{b}'$ (with sufficiently large denominators). Therefore H_2 has rank 2. Because it also has 6-fold symmetry it can only be a triangular lattice, and can therefore indeed be expressed as all integral linear combinations of two vectors $\mathbf{a}$ and $\mathbf{b}$ of equal length, 120 degrees apart.

We take $\mathbf{a}$ and $\mathbf{b}$ to be members of a set of generating vectors for the full lattice H. If we expand every vector of H in this set, and drop the two terms in which $\mathbf{a}$ and $\mathbf{b}$ appear, we get a sublattice of H of rank two less than H for which we can repeat the above procedure. Since H is of finite rank successive repetitions will yield a complete set of primitive generating vectors for H composed of pairs of vectors of equal length 120 degrees apart.

A.3 The Stacking Vectors

Because the full lattice L is closed under addition and subtraction, any plane of vectors parallel to the horizontal sublattice H must consist of H itself, shifted by a vector with a non-zero component along the axis of 3– or 6-fold symmetry. A set of primitive generating vectors for L consists of a set of primitive generating vectors

for H and a set of stacking vectors which can be regarded as primitive generating vectors for the modular lattice L/H.

To establish that the stacking vectors can be taken as specified in section 4.2, note first that the projection of L into the horizontal plane, P, is a 2-dimensional lattice with 6-fold symmetry that contains H. If $P = H$, then no stacking vectors need horizontal components. Staggered stacking vectors—those which necessarily have non-zero horizontal components—are only required if P has vectors not in H. The horizontal parts of such staggered stacking vectors can be specified by a modular lattice $P_0 = P/H$. The projected lattice P is given by the translations of P_0 through all the vectors of H, and P_0 is itself a lattice under addition modulo H. The rank of P_0 as a modular lattice is the number of independent staggered stacking vectors.

We must show that a set of generators can be found for P_0 (which generate P_0 under arithmetic modulo H) and for H, such that each generator of P_0 has the form

$$\mathbf{h} = \tfrac{2}{3}\mathbf{a}_0 + \tfrac{1}{3}r\mathbf{a}_0 \ , \tag{A.6}$$

where $\mathbf{a}_0$ and $r\mathbf{a}_0$ are a pair of primitive generators of H, r being a 120 degree rotation. For each such $\mathbf{h} \in P_0$ there is a staggered stacking vector $\mathbf{c} + \mathbf{h}$ among the primitive generators of L, which establishes our claim in section 4.2.

To establish (A.6) note first that if $\mathbf{v}$ is any vector of L with vertical and horizontal components $\mathbf{c}$ and $\mathbf{h}$, then 3-fold symmetry requires H to contain

$$\mathbf{a} = (1 - r)\mathbf{v} = (1 - r)\mathbf{h} \ . \tag{A.7}$$

H also contains

$$(1 - r^2)\mathbf{a} = (1 - r^2)(1 - r)\mathbf{h} = 3\mathbf{h}, \tag{A.8}$$

the last identity following from the fact that $1+r+r^2 = 0$ in the plane. Thus vectors in P that differ by multiples of $3\mathbf{h}$ are equivalent modulo H, as are vectors in P related by a 120 degree rotation. Consequently P_0 consists of the integral linear combinations with coefficient 1, 0, and -1 of a finite number of incommensurate vectors $\mathbf{h}_1, \ldots, \mathbf{h}_j$.

According to (A.8) any of these generators of P_0 has the form

$$\mathbf{h} = \tfrac{1}{3}(\mathbf{a} - r^2\mathbf{a}) = \tfrac{2}{3}\mathbf{a} + \tfrac{1}{3}(r\mathbf{a}) \ . \tag{A.9}$$

If $\mathbf{a}$ and $r\mathbf{a}$ are among the primitive generating vectors of H then $\mathbf{h}$ has indeed the desired form (A.6). If $\mathbf{a}$ and $r\mathbf{a}$ are not among the primitive generators of H then we can express them as integral linear combinations of a pair of primitive generating vectors, $\mathbf{a}_0$ and $r\mathbf{a}_0$:[2]

$$\begin{aligned} \mathbf{a} &= l\mathbf{a}_0 + m(r\mathbf{a}_0) \ , \\ r\mathbf{a} &= -m\mathbf{a}_0 + (l - m)(r\mathbf{a}_0) \ . \end{aligned} \tag{A.10}$$

[2]We find $\mathbf{a}_0$ and $r\mathbf{a}_0$ by examining the rank-2 sublattice of all points in H that are *rational* linear combinations of $\mathbf{a}$ and $r\mathbf{a}$, as we did in section A.2 above.

In terms of the primitive generating vectors

$$\mathbf{h} = \frac{2l-m}{3}\mathbf{a}_0 + \frac{l+m}{3}(r\mathbf{a}_0) = p\mathbf{a}_0 + q(r\mathbf{a}_0)\ . \tag{A.11}$$

Since $p+q$ is an integer, while p and q themselves are not (since $\mathbf{h}$ is not in H) there must be integers j and k such that

$$p = j \pm \tfrac{1}{3}, \quad q = k \mp \tfrac{1}{3}, \tag{A.12}$$

so that modulo H we can take $\mathbf{h}$ to be

$$\mathbf{h} = -\tfrac{1}{3}\mathbf{a}_0 + \tfrac{1}{3}r\mathbf{a}_0. \tag{A.13}$$

If we shift this by $\mathbf{a}_0$ we arrive at the desired form (A.6).