INFORMATION TO USERS

The most advanced technology has been used to photograph and reproduce this manuscript from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book. These are also available as one exposure on a standard 35mm slide or as a 17" x 23" black and white photographic print for an additional charge.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.
Topics in the physics of quasicrystals

Li, Ying-Hong, Ph.D.

The Ohio State University, 1988
TOPICS IN THE PHYSICS OF QUASICRYSTALS

DISSERTATION

Presented in Partial Fulfillment of the Requirement for
the Degree Doctor of Philosophy in the Graduate
School of the Ohio State University

By
Ying-Hong Li, B.Sc., M.S.

*****

The Ohio State University
1988

Reading Committee:
Professor T. L. Ho
Professor W. F. Saam
Professor P. E. Wigen

Approved By

Adviser
Department of Physics
ACKNOWLEDGEMENT

I would like to thank my research advisor, Professor Tin-Lun Ho, for his continuous guidance, encouragement, and support through the years. Working with him is a great experience.

Thanks are due to Professor W. F. Saam for many valuable discussions, suggestions and his critical reading of this dissertation. It has been a great pleasure to have worked in collaboration with him.

I would like to thank Professor P. E. Wigen for his guidance in my early graduate years in his lab and for his critical reading the manuscript of this dissertation.

Thanks are also due to J. Jaszczak for many useful discussion and a fruitful collaboration.

Thanks are due to many fellow graduate students for their warm friendship and useful discussions. They have made my stay here at Ohio State much more meaningful. Among them, special thanks to Dr. Pak-Ming Hui, Y. Jiang, Z. Jiang, Y. Liu, K. Chen, Y. Lu, Y, Zhu, T.-K. Xia and X.-C. Zeng. A special thank is due to Y. Jiang for her critical reading of this dissertation. I also like to thank Hong Li for her help on typing part of this dissertation.

Part of this work has been supported by NSF Grant No. DMR-8717574. The support from the Graduate School through the Graduate Student Alumni
Research Award is gratefully acknowledged.

I would like to thank for the hospitality of Institute for Theoretical Physics of University of California at Santa Barbra, Cornell University and The University of Pennsylvania. Some of my research works were either started or finished during my visits to these stimulating research institutes.

Last, but not the least, I would like to thank my parents who introduced me to physics. To my parents, this work is dedicated.
VITA

November 4, 1960 .................................. Born in Beijing, China
1983 .................................. B.Sc. Peking University,
                              Beijing, China
1983 - 1987 .................................. Graduate Teaching Associate,
                              The Ohio State University,
                              Columbus, Ohio
1985 .................................. M.S., Physics,
                              The Ohio State University,
                              Columbus, Ohio
1987 - 1988 .................................. Graduate Research Associate,
                              The Ohio State University,
                              Columbus, Ohio

PUBLICATIONS

“Faceting in Bond-Oriented Glasses and Quasicrystals”, T. L. Ho, J. Jaszczak,

“Superfluid $^3$He in Very Confined Regular Geometries”, Ying-Hong Li and
# TABLE OF CONTENTS

ACKNOWLEDGMENTS ............................................. ii
VITA .............................................................. iv
TABLE OF CONTENTS .......................................... vi
LIST OF FIGURES .............................................. x

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>I Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Overview of the Current Status of the Experimental Studies of the Quasicrystals</td>
<td>1</td>
</tr>
<tr>
<td>1.1.1 Electron Diffraction Experiments</td>
<td>3</td>
</tr>
<tr>
<td>1.1.2 High Resolution Electron Micrograph</td>
<td>10</td>
</tr>
<tr>
<td>1.1.3 X-ray Diffraction and Neutron Scattering Experiments</td>
<td>16</td>
</tr>
<tr>
<td>1.1.4 Experimental Studies on the Morphology and Other Properties</td>
<td>20</td>
</tr>
<tr>
<td>1.2 Overview of the Current Status of the Theoretical Studies of the Quasicrystals</td>
<td>23</td>
</tr>
<tr>
<td>1.2.1 Models for Structures of the Quasicrystal phases</td>
<td>23</td>
</tr>
<tr>
<td>1.2.2 The construction Schemes and Some Properties of Quasilattices</td>
<td>32</td>
</tr>
<tr>
<td>1.2.3 Some Important Properties of Quasilattices</td>
<td>38</td>
</tr>
<tr>
<td>1.2.4 Morphological Studies</td>
<td>39</td>
</tr>
</tbody>
</table>
2.5.3 X-ray Powder Diffraction Patterns ......................... 99
2.5.4 *Super rational approximates* of the decagonal perfect qua­
sicrystal ................................................................. 102

References ........................................................................ 110

III Faceting in the Icosahedral Quasicrystals and the Bond Oriented
Glasses ................................................................. 112

3.1 Introduction ............................................................. 112
3.2 Determination of the T=0 Equilibrium Shapes of Solids from
Their Surface Energies ............................................... 117
3.3 Re-examining the Origin of the Faceting Phenomena .... 122
  3.3.1 Long Range Translational Order and Facet Formation

122
  3.3.2 Cusps in Surface Energy Densities ..................... 123
  3.3.3 Conventional Derivation of Surface Energy Density  124
  3.3.4 A Sufficient Condition for Faceting in T = 0 Equilibrium
  Shapes ........................................................................ 125

3.4 T = 0 Equilibrium Shapes of the Simple Bond Oriented Sys­
tems with the Icosahedral Symmetry ............................. 129
  3.4.1 Growth Shapes and Equilibrium Shapes ............. 129
  3.4.2 Examples of the T = 0 Equilibrium and Growth Shapes
of the Simple bond Oriented Systems with the Icosahedral
Symmetry .............................................................. 131

3.5 Determination of the Surface Energies and the T=0 Equilib­
rium Shapes of the Perfect Icosahedral Quasicrystals ... 140
3.5.1 Two Dimensional Perfect Quasicrystals .......... 140
3.5.2 Three Dimensional Perfect Quasicrystals .......... 144
3.6 \( T = 0 \) Equilibrium Shapes of Quasiglasses .......... 153
References ................................................................. 158
LIST OF REFERENCES ....................................................... 159
LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURES</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1 An icosahedron with fivefold, threefold, and twofold axes labeled.</td>
<td>5</td>
</tr>
<tr>
<td>1.2 Typical experimental electron diffraction patterns of the icosahedral quasicrystal phase.</td>
<td>6</td>
</tr>
<tr>
<td>1.3 Typical experimental electron diffraction patterns of the decagonal quasicrystal phase.</td>
<td>8</td>
</tr>
<tr>
<td>1.4 A high resolution electron micrograph along a fivefold axis of a icosahedral quasicrystal phase.</td>
<td>12</td>
</tr>
<tr>
<td>1.5 A high resolution electron micrograph along the periodic axis of an octagonal quasicrystal phase.</td>
<td>14</td>
</tr>
<tr>
<td>1.6 High resolution electron micrographs along the periodic axes of dodecagonal quasicrystal phases.</td>
<td>15</td>
</tr>
<tr>
<td>1.7 A theoretical diffraction pattern along a fivefold axis of a icosahedral perfect quasicrystal.</td>
<td>25</td>
</tr>
<tr>
<td>1.8 A theoretical diffraction pattern along a threefold axis of a icosahedral perfect quasicrystal.</td>
<td>26</td>
</tr>
<tr>
<td>1.9 A theoretical diffraction pattern along a twofold axis of a icosahedral perfect quasicrystal.</td>
<td>27</td>
</tr>
<tr>
<td>1.10 The dual grid of a 2D octagonal perfect quasicrystal.</td>
<td>33</td>
</tr>
<tr>
<td>1.11 A 2D octagonal perfect quasicrystal.</td>
<td>34</td>
</tr>
<tr>
<td>2.1 An illustration of the 2D to 1D projection method.</td>
<td>55</td>
</tr>
<tr>
<td>2.2 Diffraction patterns of an 1D quasicrystal and its conventional rational approximates and super rational approximates.</td>
<td>57</td>
</tr>
</tbody>
</table>
2.3 The Wigner-Seitz cell and a portion of the 2D dodecagonal pseudo-quasicrystal ................................................................. 64

2.4 The theoretical full resolution diffraction pattern of the dodecagonal pseudo-quasicrystal. .......................................................... 67

2.5 The theoretical finite resolution diffraction pattern of the dodecagonal pseudo-quasicrystal. ......................................................... 68

2.6 An illustration of the imperfect 12-fold symmetry of the diffraction pattern shown in Figure 2.5. .................................................. 70

2.7 The theoretical X-ray powder diffraction pattern of the dodecagonal pseudo-quasicrystal. ......................................................... 78

2.8 A double-maxima peak in the theoretical X-ray powder diffraction pattern of the dodecagonal pseudo-quasicrystal with disorder. ...... 79

2.9 The Wigner-Seitz cell and a portion of the 2D octagonal pseudo-quasicrystal 82

2.10 The theoretical full resolution diffraction pattern of the octagonal pseudo-quasicrystal. ............................................................ 84

2.11 The theoretical finite resolution diffraction pattern of the octagonal pseudo-quasicrystal. ........................................................... 86

2.12 An illustration of the imperfect 8-fold symmetry of the diffraction pattern shown in Figure 2.11. ............................................... 87

2.13 The theoretical X-ray powder diffraction pattern of the octagonal pseudo-quasicrystal. ............................................................ 90

2.14 The Wigner-Seitz cell and a portion of the 2D decagonal pseudo-quasicrystal ................................................................. 92

2.15 The theoretical full resolution diffraction pattern of the decagonal pseudo-quasicrystal. ......................................................... 94

2.16 The theoretical finite resolution diffraction pattern of the decagonal pseudo-quasicrystal. .......................................................... 96
2.17 An illustration of the imperfect 12-fold symmetry of the diffraction pattern shown in Figure 2.16. ................................. 98

2.18 The theoretical X-ray powder diffraction pattern of the decagonal pseudo-quasicrystal. ......................................................... 100

2.19 The Wigner-Seitz cell and a portion of a $(2,2)^{th}$ order super rational approximate of the decagonal perfect quasicrystal. ................. 106

3.1 A triacontahedron. ................................................................. 113

3.2 A dodecahedron. ................................................................. 114

3.3 A Schematic proof of the algorithm of determining the $T = 0$ equilibrium shape. ................................................................. 120

3.4 The $T = 0$ equilibrium shape of a 2D square crystal with attractive nearest and next nearest neighbor interaction. .................. 132

3.5 A schematic illustration showing how a growth shape evolves. ... 133

3.6 The $T = 0$ equilibrium shape of the simple bond oriented system with bonds along the fivefold axes of an icosahedron. ............ 135

3.7 The $T = 0$ equilibrium shape of the simple bond oriented system with bonds along the twofold axes of an icosahedron. .......... 137

3.8 The $T = 0$ equilibrium shape of the simple bond oriented system with bonds along the threefold axes of an icosahedron. ............. 138

3.9 A set of plane-like surface in a 2D decagonal perfect quasicrystal. 141

3.10 $T = 0$ equilibrium shape of the 2D decagonal perfect quasicrystal. 145

3.11 $T = 0$ equilibrium shape of the edge model of the icosahedral perfect quasicrystal. ................................................................. 151

4.12 $T = 0$ equilibrium shape of the face model of the icosahedral perfect quasicrystal. ................................................................. 152

4.13 Comparison of a peak in the 2D decagonal perfect quasicrystal and with a peak in the 2D decagonal quasiglass. ......................... 156

4.14 A set of plane-like surfaces in the 2D decagonal quasiglass. ...... 157
CHAPTER I

Introduction

1.1 Overview of Current Status of Experimental Studies on Quasicrystals

The discovery by Shechtman et al. [1] of rapidly solidified alloys Al-M (M = Mn, Fe, Cr) producing electron diffraction patterns with sharp spots and the non-crystallographic icosahedral symmetry has stimulated intensive experimental and theoretical studies on these alloys [2]. These phases are referred as the icosahedral quasicrystal phases or simply icosahedral phases. In the literature, the term "quasicrystal" has been used rather ambiguously. On one hand, many experimentalists tend to call every alloy phase with non-crystallographic electron diffraction pattern quasicrystal. Each quasicrystal phase is further named after its non-crystallographic symmetry. For example, if the symmetry of the diffraction pattern is icosahedral, decagonal, octagonal or dodecagonal, the quasicrystal phase will be referred as the icosahedral phase, the decagonal phase, the octagonal phase and dodecagonal phase respectively. On the other hand, in most theoretical literature, quasicrystals
refer to a class of specific model structures. These are Penrose tiling types of structures which we shall define and discuss in great detail later. These structures are aperiodic arrays of “tiles” and have long range translational order. To make it clear, I shall, in this dissertation, refer these model structures as perfect quasicrystals. The term quasicrystal phases will be used in a loose sense for all alloy phases of which electron diffraction patterns have apparent non-crystallographic symmetries.

Most quasicrystal phases of alloys are formed by rapidly quenching their melts into solids. The typical cooling rate used is $10^6$ K/sec. Besides the rapidly quenching, icosahedral phases can also be obtained by using the solid reaction technique[3]. Most of the icosahedral phases are metastable. Crystallization takes place in most icosahedral phases when the samples are heated above certain temperatures. However, there are a few exceptions. Unlike the icosahedral phases of most alloys, it is recently found that the icosahedral phases of Al$_6$Li$_3$Cu and GaMgZn can be formed via slowly cooling processes with the cooling rate about 1K/sec, which is $10^6$ times slower than those used to form the icosahedral phases of most alloys. All attempts to change from the icosahedral phase to a crystalline phase by heating the Al$_6$Li$_3$Cu sample near its melting temperature are unsuccessful[5]. As we shall see later, the icosahedral phases of Al$_6$Li$_3$Cu and GaMgZn have a number of other remarkable properties.

There are three experimental techniques commonly used in studies on the structures of quasicrystal phases, namely, electron diffraction, high res-
olution electron micrograph and X-ray diffraction. The experimental results revealed by these three techniques as well as their advantages and limitations will be discussed in the next three subsections. Besides experiments on the structures, there are also experiments on the electric, magnetic, thermodynamic and morphological properties of the quasicrystals. I shall, however, discuss only briefly such experiments because only a few of them have been performed.

1.1.1 Electron Diffraction Experiments

Electron diffraction can easily reveal the apparent symmetries of solids. It can probe a small area (~1\(\mu\)m across) of the sample. It has been used to discover new non-crystallographic symmetries of these new alloy phases.

The general principle of electron diffraction is similar to that of the X-ray diffraction. For X-ray diffraction, since it only has very weakly multiple scattering, the diffraction pattern is simply proportional to the density Fourier transform of the sample. It is therefore a direct probe of the structure of the sample. However, because of electromagnetic radiation couples rather weak to matter, it becomes difficult to detect the signals of X-rays when the sample is very small, as in the case of quasicrystals. On the other hand, the electrons interact with matter much stronger than X-rays. The signals of the electron diffraction remain strong even when the sample sizes are of the order of microns. However, electron diffraction patterns relate to the density Fourier transformation in a complicated way when the multiple scattering
of electrons are important in the experiment. One way to reduce the multiple scattering of electrons is using very thin (about 200\(\mu\)m thick) samples in transmission electron diffraction experiments. In this case, the electron diffraction pattern is also proportional to the density Fourier transform of the sample.

In X-ray (or electron) diffraction patterns, each diffraction spot corresponds to a Fourier component of the density whose wave vector is perpendicular to the incident beam. Bright spots correspond to large Fourier components of the density. If the incident beam is lined up with an n-fold symmetry axis of the sample, the diffraction pattern will be n-fold symmetric.

Electron diffraction experiments are very fruitful in the studies on the structures of quasicrystal phases. The results are summarized as follows.

Using transmission electron diffraction techniques, icosahedral phases are found in rapidly quenched alloys such as Al-Mn, Al-Fe Al-Cr, Al-Mg, Al-Ru, Al-Ti, Al-Mg-Li, Ti-V-Ni, Al-Mn-Si, Pd-U-Si, Al-Li-Cu-Mg and slowly grown alloys such as Al-Li-Cu and GaMgZn. The icosahedral electron diffraction pattern has the symmetry of an icosahedron (See Figure 1.1.) It contains six 5-fold symmetry axes, ten 3-fold symmetry axes and fifteen 2-fold axes (See Figure 1.1). The experimental electron diffraction patterns of an icosahedral phase are reproduced in Figure 1.2. It is well known that icosahedral orientational symmetry is incompatible with translational symmetry.

Experiments show that all diffraction spots in the icosahedral diffraction pattern can be indexed by six-integers, \(n_0,\ldots, n_5\) and that the diffraction
Figure: 1.1 An icosahedron with 5-fold, 3-fold and 2-fold axes labeled.
Figure 1.2: Typical experimental electron diffraction patterns of an icosahedral quasicrystal phase. a) The diffraction pattern along a five-fold axis. b) The diffraction pattern along a three fold axis. c) The diffraction pattern along a two-fold axis. These diffraction patterns are reproduced from the Ref.4.
spots are located at \( k = \sum_{i=0}^{5} n_i K^{(i)} \), where \( K^{(i)} \)'s are of the same length and along the 5-fold axes of an icosahedron (See Figure 1.1). It is instructive to compare these diffraction spots with those in crystals, which are indexed by three-integers, \( n_1, n_2, n_3 \). The location of the crystal diffraction spots are given by \( k = \sum_{i=1}^{3} n_i G_i \), where \( G_i \)'s are the fundamental reciprocal lattice vectors.

Another quasicrystal phase of these alloys, now referred as the decagonal phase, was found[6] by using electron diffraction soon after the initial discovery of the icosahedral phases. The typical experimental electron diffraction patterns of the decagonal phase are shown in Figure 1.3. The diffraction patterns along the periodic directions are 10-fold symmetric. Electron diffraction patterns along the two-fold axis of the decagonal phases show that they are periodic stackings of layered structures. Each layer is a 2D quasicrystal.

Most of the decagonal phases, except that in Al-Pd, are closely related to the icosahedral phase. By slightly varying the ratio of the element concentrations and the cooling rates, the melts of these alloys can be quenched into either the icosahedral or the decagonal phases.

Other non-crystallographic electron diffraction patterns with octagonal symmetry[7] and dodecagonal symmetry[8,9] have been recently discovered in a limited number of rapidly quenched alloy phases. So far, only \( \text{Cr}_5\text{Ni}_3\text{Si}_2 \) and \( \text{V}_{11}\text{Ni}_{10}\text{Si} \) have been reported to have octagonal electron diffraction patterns. Dodecagonal electron diffraction patterns have been observed only in Ni-Cr, \( V_3\text{Ni}_2 \) and \( V_{15}\text{Ni}_{10}\text{Si} \). Both types of quasicrystal phases are periodic
Figure 1.3: Typical experimental electron diffraction patterns of a decagonal quasicrystal phase. A) The diffraction pattern along the periodic axis. B) The diffraction pattern along a twofold axis perpendicular to the periodic axis. C) The diffraction pattern along another twofold axis which is $36^\circ$ apart from the previous twofold axis and perpendicular to the periodic axis. The diffraction patterns are reproduced from Ref.16.
stackings of layer structures. It is also interesting to note that the both the octagonal and the dodecagonal electron diffraction patterns are found in rapidly quenched $V_{15}Ni_{10}Si$. We are not aware of any report on the element concentrations of this alloy and the conditions under which the two different quasicrystal phases can be formed. Together with the decagonal phase, the octagonal and the dodecagonal phases are often referred as two-dimensional quasicrystals due to their $2D$ layer structures.

Although electron diffraction is a powerful tool to study the structures of the quasicrystal phases, it has many disadvantages. As we have mentioned earlier, multiple scattering of electrons can be important in electron diffraction experiments. When multiple scattering is important, the diffraction pattern will no longer be proportional to the density Fourier transform of the sample. This makes it difficult to compare quantitatively theoretical predictions with experimental observations. Another major disadvantage of electron diffraction pattern is that the diffraction intensities are difficult to measure quantitatively. The electron diffraction pattern are usually recorded on films. At the early stage of the exposure, the brightness of a spot on the film is proportional to the intensity of the peak. However, the film will be saturated very soon and the diffraction spot will start looking diffusive. One can only qualitatively tell the relative intensities from the size of the diffraction spots on a film. The last major disadvantage is that the positions of the dominant peaks are difficult to measure precisely because the bright spots in electron diffraction patterns are often of relatively large size. As we shall
see later, a few percent inaccuracy in this measurement will result in great difficulty in distinguishing very different model structures for quasicrystal phases.

1.1.2 High Resolution Electron Micrographs

The high resolution electron micrograph is closely related to electron diffraction. In an electron diffraction experiment, the incident electron beam is diffracted by the sample. The diffracted beams are recorded on a film. The diffracted beams contain the information of the density Fourier transform of the sample. When multiple scattering of electrons can be neglected, the amplitude of the diffracted beam is proportional to the density Fourier transform of the sample. To get a high resolution electron micrograph, one replaces the film by a electron optical device which collects part of the scattered electron beams. What this device does is to inverse Fourier transform the diffraction pattern. It gives an approximate real space image of the atomic arrangement of the sample. At the same time, it also magnifies the real space structure.

There are several reasons limiting the ability of this technique to obtain quantitative structural information of the sample. Firstly, the amplitude of the diffracted beams are no longer proportional to the density Fourier transform of the sample if multiple scattering of electrons is important. Consequently, the inverse Fourier transform of the diffraction pattern is not the image of the original atomic arrangement. Secondly, usually, only part of the diffracted beams near to the central spot are collected and inverse Fourier
transformed. Fourier components with large $|k|$ are lost. Losing these large $|k|$ Fourier components makes the images of the atoms fuzzy. Although it is called high resolution electron micrograph, the images of the atoms often appear diffusive. Thirdly, due to the great magnifying power, only the images of a small portion ($\sim 200\text{Å}$ across) of the sample can be recorded on a film. In the case of an inhomogeneous sample, (e.g. one containing many domains which may have identical or different structure), the high resolution electron micrograph only shows the structure of a region which may not be representative of the entire sample.

In addition to electron diffraction patterns, high resolution micrographs of most of these quasicrystal phases have been obtained. These micrographs provide information about the homogeneities in the densities and about the atomic arrangements. Defects, such as twin boundaries and dislocations, may be observed using this method. High resolution electron micrographs can be used as a tool to directly compare the theoretical model structures and the real structures of the samples. This technique has been widely used in studies on the structures of the quasicrystals and yields many interesting results.

A typical high resolution electron micrograph along the five-fold axis of an icosahedral phase Al-Mn[10] is shown in Figure 1.4. The micrograph shows that the sample is highly homogeneous and has many ten-fold clusters (See Figure 1.4). Crystalline twin boundaries have not been observed in this micrograph. This has been considered as one evidence against the so-call
Figure 1.4: A high resolution electron micrograph along a five-fold axis of an icosahedral phase. It is reproduced from Ref.9.
"multiple twinning" model[11] of the icosahedral quasicrystal phase which we will come back to later. Holding Figure 1.4 at grazing angle, one can easily find that lines of atoms are almost quasiperiodically separated. It is noticed that these lines terminate. The terminations of these lines have been interpreted as dislocations in the perfect quasicrystal models[2].

A high resolution electron micrograph of an octagonal quasicrystal sample was reported along with its octagonal electron diffraction[7]. It is reproduced in Figure 1.5. The micrograph shows that the sample contains many octagonal rings with three atoms inside (See Figure 1.5). There is no apparent translation symmetry in the micrograph. It has been claimed that the arrangement of atoms observed in the micrograph is consistent with an octagonal *perfect quasicrystal* model structure. Eight-fold "star" atomic arrangements have also been mentioned in the paper by Wang et al.[7], although no picture was shown. These eight-fold "stars" turn out to play an important role in a model we will propose in Chapter II. It is also worthwhile to mention that there is no apparent quasiperiodicity in the micrograph.

There are only two high resolution micrographs of the dodecagonal phases reported[8,9]. In these two micrographs, many small 12-fold rings with a few atom inside have been found (See Figure 1.6). In the micrograph by Ishimasa et al.[8] (See Figure 1.6a.), these 12-fold rings are arranged on a triangular lattice. However, only a narrow strip of the micrograph is shown in this paper. Many atoms are missing inside the 12-fold rings. It is difficult to conclude from this micrograph whether the sample is a crystal or a quasicrystal. The
Figure 1.5: A high resolution electron micrograph along the periodic axis of an octagonal phase. It is reproduced from the Ref.6.
Figure 1.6: High resolution electron micrographs along the periodic axes of dodecagonal quasicrystal phases. a) A high resolution micrograph of a narrow strip of a dodecagonal phase along its periodic axis by Ishimasa et al.. It is reproduced from Ref.7. b) An electron micrograph of large portion of a dodecagonal phase along its periodic axis by Chen et al.. It is reproduced from Ref.8.
other micrograph by Chen et al. [9] (See Figure 1.6b.), contains larger portion of the sample. Inside each 12-fold ring, there is a hexagonal ring with an atom at the center. The 12-fold rings are attached together in two different ways. In one region, they are attached side by side. In another region, they penetrate each other. (See Figure 1.6b.) Both types of the arrangements extended over a range of several 12-fold rings. It is claimed by Chen et al. [9] that the later type of arrangement of the 12-fold rings is evidence of the perfect quasicrystal structure. In fact, in the next chapter, I shall show that these two types of arrangements of the 12-fold rings can be explained as parts of the crystal structures of which the diffraction patterns are almost 12-fold symmetric. No apparent quasiperiodicity, however, has been observed in the micrograph by Chen et al. either.

1.1.3 X-ray Diffraction and Neutron Scattering Experiments

X-ray diffraction experiments can be divided into two types: powder diffraction and single grain diffraction. The resolution of X-ray diffraction is much higher than that of electron diffraction experiment because the multiple scattering of X-ray are much weaker than those in electron diffraction. This is true for both X-ray powder and single grain diffraction. Since all the results of X-ray experiment on quasicrystals reported so far are from powder diffraction, we shall discuss it first.

The greatest advantage of X-ray powder diffraction over single grain diffraction is that it is much easier to prepare samples. The powder sample
contains many small grains orientated in all directions. Only the intensity as a function of |k| can be recorded, where k is the momentum transfer. The intensities as well as the positions of peaks can be measured with high accuracy.

The important results of these experiments on the icosahedral phase are summarized as follows[2]:

a. For every diffraction peak in the electron diffraction pattern of the icosahedral phase, the corresponding peak in the X-ray powder diffraction has been observed[12]. This suggests that none of the peaks in the electron diffraction pattern of the icosahedral phase result purely from the multiple electron scattering because the multiple scattering in X-ray powder diffraction are weak. This has been used as a strong criticism against the Pauling's[11] multiple twinning model for the icosahedral phase, in which the multiple scattering of electrons are crucial in explaining certain peaks in electron diffraction patterns of the icosahedral phases.

b. X-ray powder diffraction peaks can be indexed by six-integer indices[12], which is consistent with the indexing scheme of electron diffraction pattern of the icosahedral phase. Several indexing schemes have been proposed. Due to the nature of the quasicrystals, the indexing schemes of diffraction peaks are not unique[2].

c. X-ray powder diffraction peaks always have |k|-dependent finite widths which are wider than the instrumental resolution. Numerical values of these widths indicate that the correlation lengths of the quasiperiodic order in
Icosahedral samples are between 100 Å to 1000 Å. Moreover, these finite widths of the quasicrystals are almost independent of sample preparation and of materials. Such finite widths of the diffraction peaks have been referred as universal disorder [14] in quasicrystals. Conventional crystals do not have this feature.

d. The peak widths in X-ray powder diffraction have very special $|k|$-dependence. The peak width is a monotonically decreasing function of the peak intensity. The brighter a peak, the narrower is its peak width. There are explanations [14] of this phenomenon within the framework of the so-called "icosahedral glass" [23] model and the perfect quasicrystal model with disorder such as frozen "phasen" strains and dislocations. According to these models, associated with each diffraction peak, there is a unique "phasis" [13] momentum $k_\perp$. Theoretical calculation shows the peak widths of the diffraction in all these models increase monotonically with $|k_\perp|$. Their functional dependence of peak width on $|k_\perp|$ are different. X-ray experiments are in poor agreement with the prediction of the icosahedral glass model. The precision of the current experiment, however, is still not high enough to tell the nature of the disorder (i.e. whether they are frozen phason strains or dislocations).

Unlike the situation of icosahedral phase, X-ray powder diffraction [15,16] data of the decagonal phases are much less understood:

a. There are a few attempts to index X-ray powder diffraction peaks of decagonal alloy phases. None of them is successful. At the moment, it is not
clear what the correct indexing scheme should be.

b. There are many inseparable multi-maxima peak clusters in X-ray powder diffraction data[15,16]. These multi-maxima peaks are not understood at all. It seems to be difficult to explain this phenomenon within the framework of the perfect quasicrystal structure with defects.

c. Although all peaks in X-ray powder diffraction have finite widths, their $|k|$-dependences are more irregular than those in the icosahedral phases. The peak widths of some bright peaks are larger than those of weaker peaks[15,16]. It is not clear whether this phenomenon is real or an artifact of the data fitting processes (See Ref.[15] for details of data fitting).

We are not aware of any X-ray experiments on the octagonal phase or on the dodecagonal phase. At the moment, the information about the structures of the octagonal phase and the dodecagonal phase are limited to the those diffraction patterns from electron diffractions and high resolution electron micrographs, which are much less quantitative than the results of X-ray diffractions.

The main disadvantage of X-ray powder diffraction is that the information about the orientational symmetries of the samples is completely lost. The information lost in X-ray powder diffraction can be obtained in X-ray single grain diffraction. In such experiments, the diffraction intensity can be measured as a function of momentum vector $k$ to high precision. However, large single grain samples are needed for such experiments because the low X-ray scattering power. This is a serious drawback because at the present
time, large quasicrystal grains are still difficult to obtain. As a result, the data of X-ray single grain diffraction on quasicrystals is still unavailable.

Neutron scattering experiments have been performed on the icosahedral phase[17] and the decagonal phase[16]. The intensities and the positions of the neutron scattering peaks can be measured to high precision. These neutron scattering experiments yield almost the same results as X-ray powder diffraction experiments.

1.1.4 Experimental Studies on the Morphology and Other Properties

Experimental studies on the morphology of the icosahedral and decagonal phases have yielded several interesting results. Up to one and a half years ago, only micron size grains of the icosahedral phase samples had been obtained using the rapidly quenching method. The samples of the icosahedral phase are always faceted. Recently, large grains of the icosahedral phase Al₆Li₃Cu and Al-Mg have been obtained using slowly growth processes. Their growth shapes are of the form of a triacontahedron and a dodecahedron respectively. Despite of the short correlation lengths (less than 1000Å) of quasiperiodic order of the alloys, the sizes of their facets range from a few millimeters to 2 cm. This is a very puzzling fact since facets are usually assumed to be a consequence of the long range translational order. It is therefore unexpected to find facets on a scale much longer than the correlation length, where the translational order is lost. The experiments, however, tell a different
story. This brings us to a question whether the long range positional order is essential for faceting[19], which we shall discuss in Chapter III.

The morphology of the decagonal phase and other 2D quasicrystal phases is much less studied than that of the icosahedral phases.

There are also studies on the other properties of icosahedral phase, such as the electrical, the magnetic properties and the low temperature specific heat. The icosahedral phase of Mg₃Zn₃Al₂ has been reported to be superconducting below .41K[20].

In summary, we note that the majority of the experimental work in this field has focused on the determination of the structures of these new alloy phases. The structures of the icosahedral phases have been studied extensively via various techniques. Many experimental observations are consistent with perfect quasicrystal models. However, as far as we can see, the current experiments have not yet eliminated completely all the other competing models (See Section 1.2) because of their finite resolutions. There are fewer experimental studies on the 2D quasicrystal phases. Our understanding of the experimental results is poor. The electron diffraction patterns and the high resolution electron micrographs are the only known experimental results of the octagonal and the dodecagonal phases. Once again, due to limited resolution, the evidence for the octagonal and the dodecagonal quasicrystal is by no mean conclusive[21].

Experimental studies on the properties of the quasicrystal phases are still at their early stage. Large samples of quasicrystal phases are becoming
available. Hopefully, they will make X-ray single grain diffraction and other experiments on the properties of the quasicrystal phase possible.
1.2 Overview of the Current Status of the Theoretical Studies on the Quasicrystals

Numerous theoretical studies have been done on the quasicrystal phases. In this section, we shall first discuss various models proposed for the structure of quasicrystal phases. Comparison of these models to the experimental observation will be made. Among these models, the perfect quasicrystal model is the most popular one. Because of its importance and its relevance to this dissertation, the construction schemes of this model will be discussed in great detail. I shall then discuss the theoretical studies on the morphology of quasicrystals. Other theoretical studies that are less relevant to this dissertation will be mentioned only briefly.

1.2.1 Models for structures of the quasicrystal phases

Four types of models have been proposed for the structures of quasicrystals. They will be described below.

Perfect Quasicrystal Models

The Perfect quasicrystal model is also referred as a tiling model in literatures. In this model, the atoms are arranged on a perfectly ordered quasiperiodic lattice (sometimes simply referred to as a quasilattice). We shall discuss the predictions of this model and compare them with experiments. Construction schemes will be discussed later in the next subsection. The symmetry classification of the quasilattices will be only briefly mentioned in Section
1.2.3.

The quasiperiodic translational order in the quasilattices is compatible with many non-crystallographic orientational symmetries. Consequently, their density Fourier transform can have non-crystallographic point group symmetries. The electron diffraction pattern predicted by this model account for many major features, though not all, of the electron diffraction patterns.

Calculated diffraction patterns along 5-fold, 3-fold and 2-fold axes of an icosahedral perfect quasicrystal are shown in Figure 1.7 to 1.9 respectively. The following are the special features of the diffraction pattern of the icosahedral perfect quasicrystal. Many of these features are also in common to perfect quasicrystals with other symmetries.

a. Each diffraction peak in this model is a δ-function. The δ-function peak shape reflects the infinite long range quasiperiodic translational order of the icosahedral perfect quasicrystal.

b. It turns out that the diffraction spots of the icosahedral perfect quasicrystal are located at

\[ k = \sum_{i=0}^{5} m_i K^{(i)} \]  

(1.1)

where \( K^{(i)} \)'s are of the same length and along the six 5-fold axes of an icosahedron (See Figure 1.1). Each diffraction peak is labeled by six integers \( n_i, i = 0, \ldots, 5 \). This feature is unique to the quasicrystal. The reciprocal lattice of the icosahedral perfect quasicrystal can be spanned by integral linear combinations of six fundamental reciprocal lattice vectors \( K^{(i)}, i = 0, \ldots, 5 \).
Figure: 1.7 A theoretical diffraction pattern along a fivefold axis of a icosahedral perfect quasicrystal. The $\delta$-function peaks are located at the centers of the circles. The radii are proportional to the intensities of the diffraction peaks. Peak shown are only those that intensities are larger than one percent of the maximal intensity.
Figure: 1.8 A theoretical diffraction pattern along the threefold axis of a icosahedral *perfect quasicrystal*. The δ-function peaks are located at the centers of the circles. The radii are proportional to the intensities. Peaks shown are only those that intensities larger than one percent of the maximal intensity.
Figure 1.9 A theoretical diffraction pattern along the twofold axis of a icosahedral *perfect quasicrystal*. The $\delta$-function peaks are located at the centers of the circles. The radii are proportional to the intensities. Peaks shown are only those that intensities larger than one percent of the maximal intensity.
Due to the incommensuration of these six fundamental reciprocal lattice vectors, the diffraction patterns are dense with δ-functions one although they do not appear so in Figures 1.7 to 1.9. In these figures, only peaks with intensities higher than one percent of the maximal intensity are shown.

c. The last special common feature of the perfect quasicrystal model is that there are infinite many weaker diffraction peaks around any given diffraction peak. Bright peaks are, therefore, separated apart. Only a small fraction of diffraction peaks, namely those separated bright ones, can be observed in any finite resolution X-ray (or electron) diffraction experiment.

Although the theoretical diffraction pattern of this model strongly resembles the experimental electron diffraction patterns of the icosahedral phase, there are features which can not be explained by this model. For instance, the finite peak widths observed experimentally indicate that the icosahedral translational order exists only over a short range. This is contrary to the first feature of the perfect quasicrystal mentioned above. Moreover, if only the dominant diffraction spots are considered, the diffraction patterns of very different structures can be very similar[21]. The third feature above implies that only a small fraction of diffraction peaks can be observed in any given experiment due to the finite resolution. This fact raises a serious question: because of the finite resolution, to what extend can diffraction experiments alone distinguish the perfect quasicrystal structure from other competing model structures?

Icosahedral Glass Model
The icosahedral glass[23] is constructed by randomly aggregating icosahedra. During the aggregation, the icosahedra are forced to join vertex to vertex, edge to edge and face to face. There are gaps left in the resulting random structure. It is plausible that the icosahedral phases are icosahedral glasses because local icosahedral order involves low energy configurations in some alloys.

The diffraction pattern of the icosahedral glass has been calculated numerically[23]. It is in surprisingly good agreement with experiments. The diffraction peaks are very sharp. However, due to the lack of long range translational order, the peaks are no longer δ-functions. Instead, they have finite widths. The position of the diffraction peaks are given by \( k = \sum_{i=0}^{5} m_i K^{(i)} \). The corresponding phason momentum is defined as \( k_\perp = \sum_{i=1}^{5} m_i K^{(<2i>)} - m_0 K^{(0)} \), where \( <n> \) means \( n \) modular to 5.

The major advantages of this model are i) that it gives a reasonable picture of how the icosahedral phase grows from its melt and ii) that it potentially explains the the peak widths in a natural way. In this model, the peak widths are predicted to be proportional to \( |k_\perp|^{\alpha} \), where \( \alpha \geq 2[14] \). The strongest criticism to this model is that this quantitative prediction on the \( k_\perp \)-dependence of the peak widths is different from the experimental observation in which the peak widths are linearly proportional to the phason momentum \( k_\perp \).

Multiple Twinning Models

Multiple twinnings has been proposed by Pauling[11] as the model struc-
ture for icosahedral phases. In a multiple twinning model, several crystallites join together forming a cluster which has the desired non-crystallographic orientational symmetry. Each two adjacent crystallites are the mirror images of each other. The diffraction pattern of this cluster appears non-crystallographic. Multiple twinnings are low energy configurations which frequently occur in alloys. In Pauling's model the diffraction pattern of each crystallite is very different from that of the quasicrystal. The crystallites proposed usually have very large unit cells. For instance, there are more than 800 atoms in each unit cell in Pauling's models.

Pauling's multiple twinning model has received a lot of criticism. This criticism is mainly based on experimental evidence. Firstly, multiple twinnings usually lead to streaks in the electron diffraction pattern. However, no streaking has been seen in the electron diffraction pattern of the icosahedral phase. Secondly, the size of each crystallite has to be small (~20Å across). Otherwise the distinctly crystal-like diffraction patterns could have been seen in the converging beam electron diffraction experiments, which can probe a very small area (~20Å across) of the sample. Experimentally, no such crystal-like diffraction pattern has been seen in converging beam experiments. Thirdly, if the sizes of the crystallites are indeed less than 20Å, their twin boundaries should be observed in high resolution electron micrographs because micrographs can cover an area of the size of several such small crystallites. However, no twin boundaries are observed in micrographs of icosahedral phase. Finally, Pauling's multiple twinning model
requires the multiple scattering of electrons in order to explain some of the electron diffraction spots. These multiple scattering have almost been rule out experimentally (See discussion in Section 1.1.3.

Crystal with Complex Unit Cells

Crystals with complex bases have also been proposed as models for the quasicrystal phase. One naive example of this model is the so-called "rational" approximate of the perfect quasilattice. It has been estimated that such an approximate requires a unit cell containing almost $10^4$ atoms ($\sim 50\,\text{Å}$ cross)[18] in order to agree with the experimental data. Although such an example can never be ruled out as a logical possibility for the quasicrystal structure model, the extraordinary number of atoms in each unit cell makes it difficult to believe such a structure can really occur in the nature.

Recently, however, together with T. L. Ho, we have found that, at least in $1D$ and $2D$, there are many crystals with small unit cells which have X-ray and electron diffraction patterns that closely resemble those of quasicrystals[21]. The diffraction patterns of these models are in excellent agreement with some of the observed electron diffraction patterns. The multiple twinning of these crystals with small unit cells can also be used to explain some of the observed shapes of the electron diffraction peaks and the multi-maxima peaks in the X-ray powder diffraction. In my opinion, this model is not only a logical possibility but also a strong competitor for the quasicrystal structure model. Many properties of this model have not yet been explored. One of the major topics of this dissertation is to explore the details of these $2D$ models.
1.2.2 The Construction Schemes

Several schemes of producing quasilattices have been developed: they are the projection method[13,24], the dual method[25,26], the deflation-inflation method[22], and the matching rule method[22]. Among these methods, the first two are the most useful ones. We shall discuss them in detail. The last two methods will be mentioned only briefly.

The Dual Method

The dual method can generate a lattice with any symmetry. A detailed construction of a 2-dimensional eight-fold quasilattice will be given as an example to illustrate the method.

We first introduce a dual space. In this dual space, we construct a dual grid (shown in Figure 1.10). The dual grid consists of four sets of equally spaced parallel straight lines which is referred as dual grid lines. Each set of the dual grid lines are normal to one of the four direction $e_i, i = 1, ..., 4$. These lines are given by

$$\mathbf{R} \cdot \mathbf{k}^{(i)} = n_i + f_i, \quad i = 1, ..., 4$$  \hspace{1cm} (1.2)

where

$$k^{(i)} \equiv k e^{(i)} = k \left[ \cos \left( \frac{(i-1)\pi}{4} \right) \hat{x} + \sin \left( \frac{(i-1)\pi}{4} \right) \hat{y} \right].$$  \hspace{1cm} (1.3)

$f_j$ are “phase” shifts of the dual grid lines. The four sets of dual grid lines divide the dual space into polygonal regions each of which can be labeled by a set of integers \(\{n_i, i = 1, ..., 4\}\). These integers are defined as

$$n_i = \text{int}\{\mathbf{R} \cdot \mathbf{k}_i - f_i\}, \quad i = 1, ..., 4,$$  \hspace{1cm} (1.4)
Figure 1.10: The dual grid of a 2D octagonal perfect quasicrystal. See text for detail.
where \( R \) is an arbitrary point in the polygonal region, and \( \text{int} x \) is the largest integer less than \( x \). In other words, the polygonal region with integers labeled by \( n_1, \ldots, n_4 \) is contained between two lines \( n_i \) and \( n_i + 1 \) in each set. The lattice point corresponding to this polygonal region given by

\[
\mathbf{r} = \sum_{i=1}^{4} n_i \mathbf{a}^{(i)}, \quad \text{with} \quad \mathbf{a}^{(i)} = a^{(i)}.
\]

(1.5)

The resulting quasilattice (Shown in Figure 1.11) is a tiling with finite types of tiles. In this example, there are two types of tiles, a square and a 45° rhombus. The lattice points are the vertices of the tiles.

This method can be easily generated to 3-dimensional quasilattices. To get an 3D icosahedral lattice, one first constructs a 3D dual grid. It consists of six sets of equally spaced planes. Each set of planes are normal to one of the six 5-fold axes \( \{ e^{(i)}, i = 0, \ldots, 5 \} \) of an icosahedron. The dual space is divided into polyhedral regions. Eq.(1.4) can be used to determine the set of six integers \( \{ n_i, i = 0, \ldots, 5 \} \). Now \( R \) is any point in the polyhedral region. The corresponding lattice point in the icosahedral lattice is given by

\[
\mathbf{r} = \sum_{i=0}^{5} n_i \mathbf{a}^{(i)}, \quad \text{where} \quad \mathbf{a}^{(i)} = a^{(i)}, i = 0, \ldots, 5.
\]

The major advantage of this method is that it provides a very simple prescription to construct quasilattices, especially in 2D. The dual method turns out to be identical [27] to the projection method which will be discussed next.

**The Projection Method**

The projection method provides an analytic prescription of generating the quasilattices. The real space structure is obtained by projecting a strip of a
Figure 1.11: A 2D octagonal perfect quasicrystal. It is generated using the dual method. Its dual grid is shown in Figure 1.10.
higher dimensional lattice onto a physical space. (For example, a projection of a 6D to a 3D space has been used to obtain the icosahedral quasilattice.) This method has been proved to be a powerful tool in studying the diffraction properties of the quasilattices. Using this method, the diffraction patterns of quasilattices can be computed analytically.

We shall illustrate this method by considering an example in which a strip of a \( D \)-dimensional lattice is projected onto a lower \( d \)-dimensional physical space. Any lattice vector \( \mathbf{R}^{(D)} \) of the \( D \)-dimensional lattice \( \{ \mathbf{R}^{(D)} \} \) can be decomposed as \( \mathbf{R}^{(D)} = \mathbf{R}_\parallel \oplus \mathbf{R}_\perp \), where \( \mathbf{R}_\parallel \) is the component in the \( d \)-dimensional physical subspace, and \( \mathbf{R}_\perp \) is the component in the \( (D-d) \)-dimensional subspace orthogonal to the physical space. The symbol \( \oplus \) means the direct sum. The density of the projected lattice is given by

\[
\rho(r) = \int \mathcal{D}\{\mathbf{R}^{(D)}\} \delta(r - \mathbf{R}_\parallel) \delta(r_\perp - \mathbf{R}_\perp) f(r_\perp) dr_\perp, \tag{1.6}
\]

where the "acceptance" function \( f(r_\perp) \) specifying the strip to be projected is defined as

\[
f(r_\perp) = \begin{cases} 
1 & r_\perp \in C_\perp \\
0 & \text{otherwise}
\end{cases} \tag{1.7}
\]

where \( C_\perp \) is usually chosen to be the projection of the unit cell of the \( D \)-dimensional lattice onto the perpendicular subspace.

The density Fourier transform can be calculated as follows.

\[
\rho(r) = \int \mathcal{D}\{\mathbf{R}^{(D)}\} \delta(r - \mathbf{R}_\parallel) \delta(r_\perp - \mathbf{R}_\perp) f(r_\perp) dr_\perp = \int \mathcal{D}\{\mathbf{R}^{(D)}\} \delta(r \oplus r_\perp - \mathbf{R}^{(D)}) f(r_\perp) dr_\perp. \tag{1.8}
\]
Using

\[ \sum_{\{R^{(D)}\}} \delta(r \oplus r_\perp - R^{(D)}) = \frac{1}{v} \sum_{\{G^{(D)}\}} e^{i G^{(D)} \cdot R^{(D)}}, \quad (1.9) \]

where \( G^{(D)} = G_\parallel \oplus G_\perp \) is a \( D \)-dimensional reciprocal lattice vectors and \( v \) is the volume of the \( D \)-dimensional unit cell, we have

\[ \rho(r) = \frac{1}{v} \int \sum_{\{G^{(D)}\}} e^{i G_\parallel \cdot r} e^{i G_\perp \cdot r_\perp} f(r_\perp) d r_\perp \]

\[ = \frac{1}{v} \sum_{\{G^{(D)}\}} e^{i G_\parallel \cdot r} \int_{G_\perp} e^{i G_\perp \cdot r_\perp} d r_\perp. \quad (1.10) \]

From Eq.(1.10), it is easy to find that the density Fourier transform is

\[ \rho(k) = \frac{1}{v} \sum_{\{G^{(D)}\}} \delta(k - G_\parallel) \int_{G_\perp} e^{i G_\perp \cdot r_\perp} d r_\perp \quad (1.11) \]

The diffraction intensity \( I(k) \) is proportional to \( |\rho(k)|^2 \). The diffraction pattern is dense because \( \{G_\parallel\} \) is a set of infinite many integral linear combinations of \( D \) incommensurate \( k \)-vectors.

**Deflation-inflation Method and Matching Rules**

These two methods are used to generate the so-called 2D and 3D Penrose lattices. In the 2D case, it is shown by de Bruijn that they are identical to the dual method (therefore, also to the projection method). It is not clear how these methods relate to the dual method in 3D. In general, these methods are very difficult to use. Their major advantage is that the deflation-inflation method provides a natural way to use the real space renormalization group technique to study some properties of quasicrystals. On the other hand, the inflation symmetry is too restrictive to cover a wide range of quasilattices.
Readers who are interested in the details of these two methods are referred to chapter 1 of Ref. 2.

These two methods are closely tied together. They are known only for 2D and 3D Penrose lattices. However, it is difficult to calculate analytically the diffraction patterns generated by these two methods.

1.2.3 Some Important Properties of Quasilattices

An important property of the quasilattices is "local isomorphism", which can be used to classify quasilattices into classes[2]. If any finite configuration in one lattice can be found in the other lattice, these two lattices are said to be in the same isomorphism class. It can be shown that the quasilattices in the same local isomorphism class have the same diffraction pattern, diffraction intensities and energy[2].

The symmetry classification of the quasilattices has been studied using group theoretical methods. In a series of papers by Rokhsar, Mermin and Wright (RMW)[29,30], the lattice types and the space groups of the quasilattices have been classified in terms of their diffraction patterns rather than their real space structures. Before the RMW papers, there were also attempts to classify the symmetries of quasicrystal lattices. These classifications are usually done in higher dimensional crystal lattices. The projection method is then used to link the classification of higher dimensional crystal lattices to that of the lower dimensional quasilattices. The number of space groups are often over counted by using those real space methods. The correct classifi-
cation of the 3D icosahedral quasilattice by using the new scheme[29,30] is summarized as follows.

There are two icosahedral point group. One is the Y(532). The other is the $Y_h(\bar{5\,3\,m})$. There are three types of 3-dimensional quasilattices associated with each point group. They are named as simple, face-centered and body centered icosahedral lattices. There is a symmorphic space group and a non-symmorphic space group associated with each icosahedral lattice except the face-centered icosahedral lattice with point symmetry $Y_h$. Totally, there are 6 space groups associated with the point group $Y$ and 5 space groups associated with the point group $Y_h$. A table of the icosahedral space groups is given in Ref.[30].

Readers are referred to the Ref.[29] and Ref.[30] for the details of the classification of the icosahedral lattices and results of the classification of n-fold two-dimensional lattices. It is worthwhile to mention that this new classification scheme can be used in a straightforward manner to classify conventional crystals without any difficulty.

1.2.4 Morphological Studies

The experimental discoveries of the triacontahedral growth shape in Al₆Li₃Cu and dodecahedral growth shape in GaMnZn, have stimulated many theoretical studies on the $T = 0$ equilibrium shapes and the surface roughening problem of the quasicrystals. With Ho, Saam and Jaszczak[19], we have also studied the question of why the sizes of facets in the quasicrystal can
be several orders of magnitudes longer than the correlation length of the translational order.

The surface roughening of the 2D quasicrystals has been studied by several authors[31,32,33]. In these studies, the original 2D quasicrystals have been replaced by simplified models which are designed to simplify the calculation while (hopefully) capture the essential physics in 2D quasicrystals. One of these models is so-called Fabonacci tiling, which is quasiperiodic as Fabonacci sequence in one direction and is periodic in the other perpendicular direction. An important quantity characterizing the roughness of a surface is the roughening exponent \( \zeta \). It is defined as

\[
\langle (h(x + r) - h(x))^2 \rangle \sim r^{\zeta} \quad \text{as} \quad r \to \infty
\]  

where \( h(x) \) is the height of the surface at point \( x \) measured from the equilibrium surface. The symbol \( \langle \cdots \rangle \) is the thermodynamic average. A non-zero roughening exponent means the system is rough. In all 2D crystals, the roughening exponent \( \zeta = 1 \) for all non-zero temperatures and \( \zeta = 0 \) at \( T = 0 \). In contrast, it has been found that \( \zeta < 1 \) at \( T > 0 \) and continuously decreases to zero as \( T \to 0 \) in the Fabonacci tiling[31,32,33]. These analytical results have been checked numerically. The results of different methods are consistent[35]. The roughening exponent of the original Penrose tiling is not clear now at the moment. An early suggestion of non-zero roughening temperature[33] may not be true due to the failure of the mapping method used in the study[33].

The roughening problem of 3D quasilattices is much more difficult. Re-
recently, there are several attempts to solving this problem[34,35]. It has been shown that the ideal icosahedral quasicrystal is not rough at all temperatures. Disorder in the icosahedral quasicrystal makes it rough at finite temperature. The 3D decagonal quasicrystal has a finite roughening temperature.

The $T = 0$ equilibrium shapes of the icosahedral phases have been calculated recently[32,19]. Some of the predicted shapes agree with the observed growth shapes. These studies may provide some clues of the structure of the icosahedral phases. The $T = 0$ equilibrium shapes of the icosahedral phase will be discussed in Chapter III.

In a recently collaboration with T. L. Ho, W. F. Saam and J. Jaszczak, we have studied the problem of why large facets can appear in quasicrystal samples which have only short range translational order. During the course this study, we found a sufficient condition for faceting in $T = 0$ equilibrium shapes, in which the long range positional order is not required. A special class of disordered systems have been constructed as examples to show that positionally disordered systems can have facets in the $T = 0$ equilibrium shapes. These are the main topics of Chapter III.

1.2.5 Other Theoretical Studies

Theoretical studies of other properties of the quasicrystals are still in their early stages. Landau theory has been employed to show that near the melting points some of the quasicrystal phases are energetically favored over other crystalline phases[13,36,37,38]. However, the local stabilities of these qua-
sicrystal phases are not clear. Some of the theoretical studies suggest these phases are stable, and some suggest they are not\cite{39}.

Hydrodynamics modes of the quasicrystals have been studied\cite{40}. In addition to the propagating phonon modes, the phason modes are calculated. It is found that the phason modes are diffusive. However, the foundation of the hydrodynamical description of the phason modes in the quasicrystals is still questionable because the free energy of the quasicrystals might not be able to be expanded as an analytical expansion of small phason fields\cite{41}.

The magnetic, electronic and elastic properties of the quasicrystals have also been studied\cite{42}. Most of these studies are done on either 1D or 2D quasilattices. Comparisons to the experimental observations have not been made. The real space renormalization group is the most popular technique used in these studies.
1.3 Outline

The rest of this dissertation is divided into two chapters. Each of them is self contained. A class of new competing models for the 2D quasicrystals are proposed in Chapter II. The diffraction properties, the effects of disorder and the multiple twinning of these models are also discussed in Chapter II. In Chapter III, the equilibrium shapes of quasicrystals and a special class of disordered systems are discussed. An alternative sufficient condition for faceting in the $T=0$ equilibrium shapes is given there. Comparison of the theoretical predictions with the experimentally observed growth shapes are made in Chapter III. Part of Chapter II are based on a collaboration with Prof. T. L. Ho. Part of the Chapter III is based on a collaboration with Prof. T. L. Ho, Prof. W.F. Saam and Mr. J. Jaszczak.
References


[18] See footnotes 65 and 67 on page 311-312 of ref.2


[39] See page 21 and the footnote on the page in Ref. 2


[41] T. H. Ho, private communication

[42] See Chapter 7 of Ref. 2 and references therein.
CHAPTER II

Two Dimensional Crystals with Pseudo-octagonal, decagonal and dodecagonal Symmetry

2.1 Introduction

Two dimensional quasicrystal phases were discovered in rapidly quenched alloys soon after the initial discovery of the icosahedral phase. The common feature of these two dimensional quasicrystals is that there is a unique periodic axis along which layered structures are periodically stacked. The diffraction patterns along the periodic axes have non-crystallographic symmetries. The diffraction patterns along the periodic axes with 8-, 10-, and 12-fold symmetry have been reported. These quasicrystal phases are referred as the octagonal, the decagonal and the dodecagonal phase respectively. The X-ray powder diffraction was performed only on the decagonal phase. The results of the X-ray powder diffraction experiments are not well understood.

Several two dimensional quasilattices have been proposed to explain the electron diffraction patterns along the periodic directions. The $2D$ Penrose lattice has been proposed as a model structure for the $2D$ decagonal phase.
Its diffraction pattern has been calculated[1]. Although the symmetry of the calculated diffraction pattern is perfectly 10-fold symmetric, the intensity distribution of the diffraction spots is quite different from the experimental one. The diffraction pattern of an octagonal quasilattice has also been calculated[2], which agrees well with the electron diffraction pattern except that the relative intensities of a few diffraction spots are reversed. Several dodecagonal quasilattices have been proposed[3,4], but no diffraction patterns of these dodecagonal quasilattices have been calculated. The optical Fourier transform[3] of a large portion of one of these dodecagonal quasilattices shows significant deviations from the electron diffraction pattern[5]. (In an optical Fourier transform, the lattice pattern is first recorded on a microfilm. Then a laser beam is shined to the microfilm. The diffracted laser beams are collected by a set of optical lenses. This optical device Fourier transforms the lattice pattern and focuses the pattern of the Fourier transform on another film). So far, most of these 2D quasicrystal models have not satisfactorily explained the experimental observations.

On a close examination of the high resolution electron micrographs[7,5] of the dodecagonal phase, we have recently noted that they show features of crystals. There are two different crystal structures in the micrograph in small ranges. Both of them have the same triangular Bravais lattice. The detailed structures of the crystals are given in section 2.3.

Motivated by these observations, we have studied the diffraction patterns of these crystals[8]. We have found that the diffraction pattern of one of them
is surprisingly similar to the observed electron diffraction pattern along the periodic axis. Moreover, for a wide range of resolutions in the intensities and the positions of the diffraction spots, (discussed later in this chapter), the diffraction pattern of this crystal is indistinguishable from the experimental electron diffraction pattern[5] of the dodecagonal phase.

The most remarkable property of this model, however, is that there are only 13 atoms in the unit cell. This small size of the unit cell runs counter to the common belief of that only crystals with extremely large unit cells can have diffraction patterns similar to those of quasicrystals phases. Recently, some previous rough estimates even show that crystals with large unit cells containing $10^4$ atoms[6] are needed to make diffraction patterns similar to those of a quasicrystal phase. This estimate is based on certain model crystal structures which do not include our model.

The success in the dodecagonal case has led us to similar investigations on 2D quasicrystal phases with 8-fold and 10-fold symmetries. We have studied many possible crystal structures for the 2D decagonal phase. We have found a crystal structure with a 36° rhombic Bravais lattice. Its unit cell contains 18 atoms. A finite resolution diffraction pattern predicted by this model agrees very well with the electron diffraction pattern of AlPd decagonal phase[9] except for the shapes of diffraction spots. As for the octagonal phase, we have also constructed a crystal structure with a 14-atom unit cell, which produces an almost 8-fold symmetric diffraction pattern. However, the comparisons to the experimental electron diffraction pattern are less satisfactory than what
we expected.

In the rest of this dissertation, these new crystal structures are referred as the n-fold pseudo-quasicrystals. The structures, the diffraction patterns, and other properties of the 8-fold, 10-fold and 12-fold pseudo-quasicrystal will be discussed in section 3.3, 3.4, and 3.5. The question which naturally arose is why the diffraction pattern of these crystals are so quasicrystal like. The mechanism causing this phenomenon turns out to be quite general. It appears even in the 1D case. This mechanism in 1D is explained in the next section to provide an example of the general framework. Some necessary terminologies will be introduced first.
2.2 Crystals with Incommensurate Bases and the Resonance Condition

Consider a crystal which has a the Bravais lattice spanned by three fundamental lattice vectors \( \{ \mathbf{a}_i, i = 1,2,3 \} \). (In 2D case, there are only two fundamental lattice vectors). There are \( l \) atoms in the unit cell located at \( \{ \mathbf{c}_j, j = 1,...,l \} \). The density of this crystal is

\[
\rho(\mathbf{r}) = \sum_{\{n_i\}} \sum_{j=1}^{l} \delta(\mathbf{r} - (\sum_{i=1}^{3} n_i \mathbf{a}_i + \mathbf{c}_j)).
\]  

(2.1)

The locations of the base atoms can be expressed in terms of \( \{ \mathbf{a}_i \} \), i.e.

\[
\mathbf{c}_j = \sum_{i=1}^{3} \alpha_{ij} \mathbf{a}_i, \quad \text{where} \quad 0 \leq \alpha_{ij} < 1.
\]  

(2.2)

If any of these \( \alpha_{ij} \)'s are irrational numbers, the basis is referred as an incommensurate basis. Otherwise, it is referred as a commensurate basis. It is important to note that a crystal with an incommensurate basis is different from an incommensurate crystal in which there are two or more incommensurate periodicities.

The density Fourier transform of a crystal with incommensurate basis can be calculated in a straightforward manner. The result is given by

\[
\rho(\mathbf{k}) = \sum_{\{n_i\}} \delta(\mathbf{k} - \sum_{i=1}^{3} n_i \mathbf{G}_i)w(\mathbf{G}),
\]  

(2.3)

where

\[
\mathbf{G}_i \cdot \mathbf{a}_j = 2\pi \delta_{ij}
\]
Since some of \( \alpha_{ij} \)'s are irrational, the diffraction pattern \( I(\mathbf{k}) = |\rho(\mathbf{k})|^2 \) is not a periodic function of \( \mathbf{k} \), although all nonvanishing spots are located on a periodic array in \( \mathbf{k} \)-space.

From Eq.(2.4), we find that the bright diffraction peaks appear at those \( \mathbf{G} \) such that all atoms in a unit cell scatter coherently. In other words, all quantities \( \mathbf{G} \cdot \mathbf{c}_j \)'s are close to each other apart from a multiple of \( 2\pi \). Without losing generality, one of the \( \mathbf{c}_j \)'s can be chosen as zero. With this choice, the condition for being a bright spot is that all \( \mathbf{G} \cdot \mathbf{c}_j \)'s are close to zero, i.e.

\[
\sum_{j=1}^{l} \alpha_{ij} \approx 0 \quad j = 1, \ldots, l, \tag{2.5}
\]

where \( |\delta_j| \ll 1, \quad j = 1, \ldots, l \). Since \( \alpha_{ij} \) is an irrational number, the integers \( n_i \)'s satisfying Eq.(2.5) are not periodically distributed in the real number axis. Consequently, even in an infinite resolution diffraction pattern, these bright spots do not appear periodically in \( \mathbf{k} \)-space although the underlying \( \mathbf{k} \)-space is periodic. In a finite resolution diffraction pattern, only diffraction spots with intensities above certain threshold can be observed. The weak spots in the underlying periodic lattice will not be observable. As a result, therefore, the diffraction pattern will appear to be aperiodic. In fact, we shall
show that the finite resolution diffraction patterns of some of these crystals with incommensurate bases can be very similar to those of quasicrystals.

Let's first consider a theoretical model of 1D quasicrystal constructed using the projection method. It is obtained by projecting the 2D lattice points inside an "irrational" strip onto a 1D physical space. This physical space is a 1D straight line embedded in a 2D space, which is parallel to the irrational strip. Let $\theta$ be the angle between the strip and the basis vector $e_1$ of the square lattice (See Figure 2.1). An irrational strip is defined to be a strip where the $\tan \theta$ is irrational. Similar, a rational strip is the one where $\tan \theta$ is rational.

The structure of this 1D quasicrystal is given by (see section 1.2.2)

$$\rho(r) = \int \sum_{n_1,n_2} \delta(r - (n_1c + n_2s)A)\delta(r - (-n_1s + n_2c)A)f(r_\perp)dr_\perp, \quad (2.6)$$

where

$$f(r_\perp) = \begin{cases} 1 & 0 \leq r_\perp < (s + c)A, \\ 0 & \text{otherwise} \end{cases}, \quad (2.7)$$

and $s \equiv \sin \theta$, $c \equiv \cos \theta$. $\alpha \equiv s/c$ is an irrational number. Using Eq. (1.11), we have the diffraction intensity

$$I(k) = |\rho(k)|^2$$

$$I(k) = \frac{1}{A^2} \left| \sum_{n_1,n_2} \delta(k - (n_1c + n_2s)) \frac{2\pi}{A} \int_0^{(s+c)A} e^{i(-n_1s+n_2c)2\pi r_\perp}dr_\perp \right|^2$$

$$= \sum_{n_1,n_2} \delta(k - (n_1c + n_2s)) \frac{\sin^2(\pi(-n_1s+n_2c)(s+c))}{\pi^2(-n_1s+n_2c)^2}. \quad (2.8)$$

The condition for bright diffraction spot is

$$|-n_1s + n_2c| \ll 1, \quad (2.9)$$
Figure 2.1: An illustration of the 2D to 1D projection method. The 1D quasicrystal is constructed by projecting the strip of square lattice between two solid lines onto the irrational physical space (one of the solid lines). The strip of square lattice between two dashed lines is projected onto the same irrational physical space to produce a super rational approximate.
i.e.

\[ n_1 \alpha = n_2 + \alpha \delta, \quad \text{with} \quad |(\alpha \delta)| \ll 1. \quad (2.10) \]

So, the bright diffraction spots appear at

\[ k = \left( n_2 \frac{c^2}{\delta} + n_2 s + c \delta \right) \frac{2\pi}{A} \]
\[ = \left( n_2 + c \delta \right) \frac{2\pi}{A}. \quad (2.11) \]

The intensity of this bright spot is

\[ I(k) = (s + c)^2 \left\{ 1 - \frac{1}{3} (\pi s \delta)^2 (s + c)^2 + O(\delta^4) \right\}. \quad (2.12) \]

A 1D Fibonacci quasilattice is obtained by choosing \( \alpha = 1/\tau \), where \( \tau = (\sqrt{5} + 1)/2 \) is the golden mean. The diffraction pattern of the 1D Fibonacci quasilattice is shown in Figure 2.2.

Next, we consider a special class of crystals with incommensurate bases, which are referred as "rational approximates" of quasicrystals. A rational approximate of a 1D quasicrystal is defined to be the projection of the 2D lattice points inside a rational strip onto a straight line. Let us consider two special choices of this line. The first one is a line parallel to the rational strip, and the second one is a line parallel to the original physical space of the quasicrystal. The crystals obtained by the first and the second choices are referred as the conventional rational approximates and the super rational approximates respectively.

The order of the rational approximates of quasicrystals can be defined according to the slope of the rational strip regardless which 1D physical
Figure 2.2: Diffraction patterns of an 1D quasicrystal and its rational approximates. From top: The lowest order super rational approximate with 2 atoms per unit cell, the second lowest order super rational approximate with 3 atoms per unit cell, 1D Fibonacci quasicrystal, a conventional rational approximation with 34 atoms per unit cell, a conventional rational approximate with 21 atoms per unit cell.
space is used. Before we define the orders of the rational approximates, some necessary results of elementary number theory are introduced first.

Any given irrational number $x$ uniquely defines a continued fraction of the following form

$$x = a_0 + \frac{1}{a_1 + \frac{1}{a_2 + \ldots}}$$

(2.13)

where all $\{a_i\}$ are integers. $[a_0a_1a_2\ldots a_n\ldots]$ is a commonly used short notation for the continued fraction in Eq. (2.13). If all terms after $a_n$ are dropped, the continued fraction becomes a finite term continued fraction $[a_0a_1a_2\ldots a_n]$. $[a_0a_1a_2\ldots a_n]$ is a rational approximate of the irrational number $x$. It can be expressed as $p_n/q_n$ where $p_n$ and $q_n$ are mutually prime integers. These $p_n/q_n$'s form a sequence which approaches the limit $x$. It is well known that any given irrational number can be approached by sequences of rational numbers. It turns out that the sequence given by the continued fraction is the best one in the sense that each term in this sequence has the least error within the family of all the rational approximates with the same integer denominator. For this reason, we shall only define the orders for those rational approximates in which the rational slope is a term in the sequence determined by the continued fraction.

Suppose that the irrational slope in the quasicrystal is $x = [01a_2\ldots a_n\ldots]$ where $x < 1$. If the rational slope $\alpha = p_n/q_n$ is the $n^{th}$ term in the rational sequence determined by the continued fraction $[01a_2\ldots a_n\ldots]$, the order of the rational approximate of the quasicrystal is said to be $n$. It turns out that the lowest order rational approximate of a quasicrystal is the one with the
slope $\alpha = 1$.

Let us consider the lowest order super rational approximate which is a crystal structure with a two-atom unit cell. Its lattice constant is $(s + c)A$, where $A$ is the lattice constant of the $2D$ square lattice. This crystal structure given by

$$\rho(r) = \sum_n \{\delta(r - n(s + c)A) + \delta(r - n(s + c)A - sA)\}, \quad (2.14)$$

where $s = \sin \theta, \quad c = \cos \theta$.

The angle $\theta$ is same as that in the quasicrystal case. It is straightforward to find that its density Fourier transform is

$$\rho(k) = \sum_m \delta(k - m(\frac{2\pi}{(s + c)A})) \cos^2(\frac{\pi m \alpha}{1 + \alpha}), \quad \text{with} \quad \alpha = s/c. \quad (2.15)$$

Bright diffraction spots occur when its $k$ satisfy the following “resonance” condition:

$$\frac{m \alpha}{1 + \alpha} = n + \epsilon, \quad (2.16)$$

where $n$ is an integer, and $|\epsilon|$ is a very small number. This condition can be rewritten as

$$(m - n)\alpha = n + (1 + \alpha)\epsilon. \quad (2.17)$$

For a sufficiently bright spot, the $\epsilon$ is small enough so that $|(1 + \alpha)\epsilon|$ is very small. Therefore, condition Eq.(2.17) is identical to the condition Eq.(2.10) if we make the identification $(m - n)$ to $n_1$ and $n$ to $n_2$. The bright spot in the diffraction pattern of the crystal appears at

$$k = m\frac{2\pi}{(s + c)A} = (n + \epsilon)(1 + 1/\alpha)\frac{2\pi}{(s + c)A}$$
\[ n \frac{2\pi}{A_s} + \frac{2\pi}{A_s} \]  

(2.18)

Its intensity \( I(k) \) is

\[
I(k) = |\rho(k)|^2 = 1 - \epsilon^2 + O(\epsilon^4),
\]

(2.19)

where \( I_0' \) is a prefactor determined by the scattering cross section of the crystal. If we identify \( n = n_2 \), the positions of the two corresponding bright spots differ only by a very small amount of \((\epsilon - \delta c)(2\pi/A_s)\). Both intensities are close to each other. Figure 2.2 shows the comparison of the two diffraction patterns. One can easily find that the diffraction pattern of the crystal closely resembles that of the quasicrystal over the entire \( k \)-space. The diffraction pattern of the next lowest order super rational approximate is also shown in Figure 2.2. The slope of the rational strip is 1/2. There are three atoms per unit cell.

The crystal structure of the conventional rational approximate is obtained by projecting the 2D lattice points in a rational strip onto a straight line with the same slope of the rational strip. (The is usual rational approximates referred in the literatures). Suppose that the slope is \( \alpha = \frac{p}{q} \). The lattice constant of the 1D crystal structure is \( a = (p^2 + q^2)^{\frac{1}{2}} A \), where \( A \) is the lattice constant of the 2D square lattice. There are \( p + q \) atoms in the unit cell. Their locations are

\[
c_j = \frac{l_jq + m_jp}{(p^2 + q^2)^{\frac{1}{2}}} A
\]
where \( l_j \) and \( m_j \) are integers. This is a crystal with commensurate basis all the coefficients \( \{ \frac{l_j q + m_j p}{p^2 + q^2} \} \) are rational numbers. The density of this crystal is given by

\[
\rho(r) = \sum_{n} \sum_{j=1}^{p+q} \delta(r - (na + c_j)).
\]

(2.21)

The density Fourier transform \( \rho(k) \) can be calculated in a straightforward manner. The result is

\[
\rho(k) = \sum_{n} \sum_{j=1}^{p+q} \delta(k - \frac{2\pi}{a}) e^{i2\pi n(c_j/a)}
\]

\[
= \sum_{n} \sum_{j=1}^{p+q} \exp\{i2\pi n(l_j q + m_j p) / (p^2 + q^2)\}.
\]

(2.22)

Eq.(2.22) shows \( \rho(k) \) is also a periodic function of \( k \) with the period \((p^2 + q^2)^{2\pi}/A\). Consequently, the diffraction pattern \( I(k) = |\rho(k)|^2 \) is a periodic function of \( k \). The periodicity shows up in the diffraction pattern covering a large region of the \( k \)-space. Although this diffraction pattern agrees reasonably well with that of the quasicrystal within its first period, the two diffraction patterns are easy to distinguish over a large region of \( k \)-space.

In principle, one can use very high order conventional rational approximates to get better agreement between their diffraction patterns and that of the quasicrystal. However, the unit cells of such high order conventional rational approximates to be extremely large for a good agreement over a large region of the \( k \)-space. Moreover, even the diffraction patterns of high order conventional rational approximates do not agree that of the quasicrystal not
as well as those of low order super rational approximates. We have included the diffraction patterns two high order conventional rational approximates in the Figure 2.2 to illustrate this phenomenon. The slopes 5/8 and 13/21 are used in the constructions of these crystal structures. There are 21 and 34 atoms in each unit cell respectively. Large differences between the diffraction patterns of the high order conventional rational approximates and those of the quasicrystal show up in the large $k$ region, while those of the low order super rational approximates keep approximate the diffraction pattern of the quasicrystal well in the entire observable $k$-space.

At the end of this Beet ion, we want to emphasize that the diffraction patterns of crystals with incommensurate bases can be very similar to those of quasicrystals although their real space structures can be very different. The key mechanism responsible for this is the resonance in the crystals with incommensurate bases. This is also why super rational approximates are so superior to conventional rational approximates when their diffraction patterns are compared with those of the quasicrystals which they approximate. This phenomenon is generic in all crystals with incommensurate bases. It is not a special property of one-dimensional space. It is general for all dimensions with only slight modifications.
2.3 The Dodecagonal Pseudo-quasicrystal

As we have discussed, at the beginning of this chapter, many features of the 2D quasicrystal phases are very difficult to understand within the framework of the quasicrystal models. On the other hand, high resolution electron micrographs of the dodecagonal phase show signs of crystal structures. Motivated by this observation, we have studied the diffraction patterns of the crystals suggested by the electron micrographs. We succeeded in finding a crystal with small unit cell which mimics the experimental electron diffraction pattern very well. Our model also predicts that there are peaks with double-maxima in the X-ray powder diffraction pattern, (a general feature found in icosahedral phase). We shall discuss our model and its implications in detail in this section. We have done similar work on the octagonal phase and the decagonal phase. This will be presented in the next two sections.

2.3.1 Model Structure

The model structure of the dodecagonal pseudo-quasicrystal is a triangular lattice with a 13-atom basis. It is shown in Figure 2.3a. The two primitive lattice vectors are

\[ \mathbf{a}_1 = (2 + \sqrt{3})A \left( \frac{\sqrt{3}}{2} \hat{x} - \frac{1}{2} \hat{y} \right) \]
\[ \mathbf{a}_2 = (2 + \sqrt{3})A \hat{y}. \]
Figure 2.3: The Wigner-Seitz cell and a portion of the 2D dodecagonal pseudo-quasicrystal. 
a) A Wigner-Seitz cell of the dodecagonal pseudo-quasicrystal.
b) A portion of the dodecagonal pseudo-quasicrystal.
The Wigner-Seitz cell is also shown in Figure 2.3b. The locations of the atoms in a Wigner-Seitz cell are:

\[ c_0 = 0 \]

\[ c_j = A(\cos((j - \frac{1}{2}) \frac{\pi}{3})\hat{x} + \sin((j - \frac{1}{2}) \frac{\pi}{3})\hat{y}), \quad j = 1, \ldots, 6 \]

\[ c_j = (2 + \sqrt{3})^3 A(\cos((j - \frac{13}{2}) \frac{\pi}{6})\hat{x} + \sin((j - \frac{13}{2}) \frac{\pi}{6})\hat{y}), \quad j = 7, \ldots, 18. \] (2.24)

There are only 13 atoms in each unit cell because each of the 12 atoms on the dodecagonal outer ring is shared by two Wigner-Seitz cells. This Wigner-Seitz cell structure occurs very frequently in the high resolution electron micrograph of the dodecagonal phase[5]. One may have already noticed that rotating the Wigner-Seitz cell by 30° is identical to rotating the hexagonal inner ring by 30°. After such rotation, the cell still fits the lattice perfectly. This feature will be used later when we discuss the disorder in the dodecagonal pseudo-quasicrystal.

### 2.3.2 Electron Diffraction Patterns

The density of this dodecagonal pseudo-quasicrystal can be written as

\[ \rho(r) = \sum_{n_1, n_2} \left\{ \sum_{j=0}^{6} \delta(r - (n_1a_1 + n_2a_2 + c_j)) + \frac{1}{2} \sum_{j=7}^{18} \delta(r - (n_1a_1 + n_2a_2 + c_j)) \right\}. \] (2.25)

Its diffraction \( I(k) \) is given by

\[ I(k) = |\rho(k)|^2 = \sum_{n_1, n_2} \delta(k - (n_1G_1 + n_2G_2)) |w(k)|^2, \] (2.26)
where the structure factor is

\[ w(k) = 1 + \sum_{j=1}^{6} e^{i k \cdot e_j} + \frac{1}{2} \sum_{j=7}^{18} e^{i k \cdot e_j}, \quad (2.27) \]

and the primitive reciprocal lattice vectors are defined as

\[ G_1 = \frac{2\pi}{(2 + \sqrt{3})A\sqrt{3}} \hat{x} \]
\[ G_2 = \frac{2\pi}{(2 + \sqrt{3})A\sqrt{3}} \left( \frac{1}{\sqrt{3}} \hat{x} + \hat{y} \right). \quad (2.28) \]

A full resolution diffraction pattern is shown in Figure 2.4. The periodicity of the crystal shows up as a triangular lattice in \( k \)-space. The basis vectors in real space can be determined from the full resolution diffraction pattern. However, if the threshold is raised to \( 0.12I(0) \), (i.e. only diffraction peaks with intensities greater than 12\% of the maximal intensity can be seen), the diffraction pattern will look almost 12-fold symmetric (see Figure 2.5), even though the exact symmetry is 6-fold.

To show the imperfect 12-fold symmetry of the finite resolution diffraction pattern in Figure 2.5, Figure 2.5 is rotated by 30\° and is superimposed to the original one as shown in Figure 2.6. The deviations show up as in the mismatches. Figure 2.6 clearly shows that the deviation from a 12-fold symmetric pattern is very small. A notable property of the diffraction pattern is that diffraction spots with large intensities form almost 12-fold symmetric rings. The higher the intensity, the closer to the perfect 12-fold symmetry.
Figure 2.4: The theoretical full resolution diffraction pattern of the dodecagonal pseudo-quasicrystal. $\delta$-function peaks are located at the centers of the circles. The radii are proportional to the diffraction intensities. For peaks with intensities less than $0.01I(0)$, the size of the circles are uniform.
Figure 2.5: The theoretical finite resolution diffraction pattern of the dodecagonal pseudo-quasicrystal. Only peaks with intensity larger than $0.12I(0)$ are shown. δ-function peaks are located at the centers of the circles. The radii are proportional to the diffraction intensities.
For diffraction spots with larger intensities, the two patterns will have better agreement.

Comparing Figure 2.5 with the experimental electron diffraction pattern[5] shows that it accounts for all the experimental diffraction spots, except a few very diffuse ones. The positions of the diffraction spots in the experimental pattern have been carefully measured. The positions of the diffraction spots in our theoretical pattern agree with those of the experimental pattern within 1%. However, as we have discussed in section 1.1.1, it is almost impossible to measure the diffraction intensities from the electron diffraction pattern. We are therefore unable to make any quantitative comparison between the theoretical diffraction intensities and the experimental ones. Nevertheless, the two diffraction intensity distributions qualitatively agree with each other.

Figure 2.6 can be regarded as the diffraction pattern of a 30° twin of the dodecagonal pseudo-quasicrystals in which crystallites scatter incoherently. As we have discussed, within a wide range of resolutions, the diffraction pattern of the dodecagonal pseudo-quasicrystal is excellent in agreement with those observed in the dodecagonal phase. Figure 2.6 shows that the twin of the dodecagonal pseudo-quasicrystals does not change the diffraction pattern much. We feel it is completely unnecessary to introduce this twin to explain to experimental electron diffraction patterns of the dodecagonal phase.
Figure 2.6: An illustration of the imperfect 12-fold symmetry of the diffraction pattern shown in Figure 2.5. Mismatches of the circles show the imperfectness of the symmetry. Only peaks with intensity larger than $0.2I(0)$ are shown. $\delta$-function peaks are located at the centers of the circles. The radii are proportional to the diffraction intensities.
2.3.3 Why Are These Finite Diffraction Patterns so 12-fold Symmetric?

As we have seen in Figure 2.5, the finite resolution diffraction pattern of the dodecagonal pseudo-quasicrystal differs only slightly from a perfectly 12-fold symmetric one. The nearly perfect 12-fold symmetry is related to the fact that for every bright diffraction spot located at $G$ of intensity $I(G)$, there exists another bright spot with very close intensity and located close to $TG$. $T$ is the rotation about the $z$-axis by $2\pi/12$. This phenomenon is an analogue of the resonance in the $1D$ case discussed in the section 3.2.

Consider an arbitrary diffraction spot at $G = n_1G_1 + n_2G_2$. Its intensity $I(G)$ is given by

$$I(G) = 1 + 2 \cos\left(\frac{6\pi}{\sqrt{3}}n_1\right) + 2 \cos\left(\frac{6\pi}{\sqrt{3}}n_2\right)$$
$$+ 2 \cos\left(\frac{6\pi}{\sqrt{3}}(n_1 - n_2)\right) + 2 \cos\left(\frac{2\pi}{\sqrt{3}}(-n_1 + n_2)\right)$$
$$+ 2 \cos\left(\frac{2\pi}{\sqrt{3}}(-2n_1 + n_2)\right) + 2 \cos\left(\frac{2\pi}{\sqrt{3}}(n_1 + n_2)\right). \quad (2.29)$$

The condition for the bright diffraction spots is

$$\frac{n_1}{\sqrt{3}} = m_1 + \epsilon_1,$$
$$\frac{n_2}{\sqrt{3}} = m_2 + \epsilon_2, \quad (2.30)$$

where $m_1$, $m_2$ are integers and $|\epsilon_1|, |\epsilon_2| \ll 1$. So, the intensity is very close to the maximal intensity.

For any reciprocal lattice vector $G = n_1G_1 + n_2G_2$, after a $30^\circ$ rotation
about z-axis, we have

\[ \mathbf{G} \rightarrow \mathbf{k}' = \frac{2n_1 - n_2}{\sqrt{3}} \mathbf{G}_1 + \frac{n_1 + n_2}{\sqrt{3}} \mathbf{G}_2. \]  

(2.31)

The resulting vector \( \mathbf{k}' \) is not a reciprocal lattice vector. However, for a bright diffraction spot, using Eq. (2.30), we have

\[ \mathbf{k}' = (2m_1 - m_2)\mathbf{G}_1 + (m_1 + m_2)\mathbf{G}_2 
\quad + (2\epsilon_1 - \epsilon_2)\mathbf{G}_1 + (\epsilon_1 + \epsilon_2)\mathbf{G}_2. \]  

(2.32)

Although \( \mathbf{k}' \) is not a reciprocal lattice vector, it differs from another reciprocal lattice vector \( \mathbf{G}' = (2m_1 - m_2)\mathbf{G}_1 + (m_1 + m_2)\mathbf{G}_2 \) only by a small amount of the order of \( \epsilon \). We shall refer the diffraction spots at \( \mathbf{G} \) and \( \mathbf{G}' \) as almost symmetry related pair.

The intensity of the diffraction peak at \( \mathbf{G}' \) is given

\[ I^{1/2}(\mathbf{G}') = 1 + 2 \cos(2\pi\sqrt{3}(2m_1 - m_2)) \]
\[ + 2 \cos(2\pi\sqrt{3}(m_1 + m_2)) + 2 \cos(2\pi\sqrt{3}(m_1 - m_2)) \]
\[ + 4 \cos(2\pi\sqrt{3}m_1) + 2 \cos(2\pi\sqrt{3}(-m_1 + m_2)). \]  

(2.33)

Using Eq. (2.30), we have

\[ \sqrt{3} m_1 = n_1 - \sqrt{3} \epsilon_1 \]
\[ \sqrt{3} m_2 = n_2 - \sqrt{3} \epsilon_2. \]  

(2.34)

Therefore the intensity can be written as

\[ I^{1/2}(\mathbf{G}') = 1 + 2 \cos(2\pi\sqrt{3}(2\epsilon_1 - \epsilon_2)) \]  

(2.35)
Both $\epsilon$'s multiplied by $\sqrt{3}$ are still very small. Therefore, the intensity of the diffraction spot at $G'$ is also very close to the maximal intensity. This means that the diffraction intensities of the symmetry related pair are very close.

### 2.3.4 Disorder in the Dodecagonal Pseudo-quasicrystals

Rapidly quenched alloys are usually highly disordered. In general, the presence of disorder broadens the diffraction peaks and even destroys the point group symmetry of the different pattern. However, in the dodecagonal pseudo-quasicrystal there is a special class of disorder which affects the bright diffraction peaks only by broadening them from $\delta$-function shapes into Gaussian ones with finite peak widths.

As we mentioned before, rotating an inner hexagonal ring in a Wigner-Seitz cell does not introduce mismatches in the dodecagonal pseudo-quasicrystal. This operation is equivalent to interchanging the squares and triangles between the inner and outer rings. No new types of atomic bonds are created by this operation.

A class of disorder can be described by randomly rotating the inner hexagonal rings by $30^\circ$. The resulting crystal structure with disorder is given by

$$
\rho(r) = \sum_{\mathbf{R}} \{ \delta(r - \mathbf{R}) + \frac{1}{2} \sum_{j=1}^{18} \delta(r - (\mathbf{R} + \mathbf{c}_j)) \} 
$$

(2.36)
\[ + \sum_{j=1}^{6} [P_{R} \delta(r - (R + c_{j})) + (1 - P_{R}) \delta(r - (R + T c_{j}))], \]

where \( R \) sum over the entire triangular lattice. \( T \) is a 30° rotation about the \( z \)-axis. \( P_{R} \) is an integer randomly taking value 0 or 1, representing the inner hexagonal ring is rotated or unrotated.

There is no change in nearest neighbor atomic bonds. Therefore, disorder of this type is very easy to form in the case of only nearest neighbor interaction.

The diffraction pattern of the dodecagonal quasicrystal with disorder of this type can be calculated as follows. The first two terms in Eq.(2.37) can be Fourier transformed directly. So, we have the density Fourier transform

\[ \rho(k) = \frac{N}{V} \sum_{G} \left[ (1 + \frac{1}{2} \sum_{j=1}^{18} e^{iG \cdot c_{j}}) \delta(k - G) \right. \]
\[ \left. + \frac{1}{V} \left\{ \sum_{R} e^{i\mathbf{k} \cdot \mathbf{R}} \left[ P_{R} \sum_{j=1}^{6} e^{i\mathbf{k} \cdot c_{j}} + (1 - P_{R}) \sum_{j=1}^{6} e^{i\mathbf{k} \cdot T c_{j}} \right] \right\} \right], \]

where \( V \) is the total volume of the sample. The volume of a unit cell is denoted by \( v \). The diffraction intensity of the dodecagonal pseudo-quasicrystal with disorder is given by

\[ I(k) = \rho(k) \rho(-k) \]
\[ = \frac{1}{v^2} \sum_{G} |w(G)|^2 \delta(k - G) \]
\[ + \frac{1}{V} \left\{ N \sum_{G} \delta(k - G) w(G) w_1(-k) \sum_{R} P_{R} e^{-i\mathbf{k} \cdot \mathbf{R}} + c.c. \right\}. \]
Form now on, we drop the prefactor $I_0$ in the diffraction intensities for simplicity. Having taken the ensemble average, we have the diffraction density

$$< I(k) > = \frac{1}{v^2} \sum_{G} |w(G)|^2 \delta(k - G)$$

$$+ \frac{1}{V^2} \left\{ N \sum_{G} \delta(k - G) w(G) w_1(-k) \sum_{R} < P_R > e^{-ikR} + c.c. \right\}$$

$$+ \frac{1}{V^2} \left\{ N \sum_{G} \delta(k - G) w(G) w_1'(-k) \sum_{R} < 1 - P_R > e^{-ikR} + c.c. \right\}$$

$$+ w_1(k) w_1'(-k) \sum_{R, R'} < P_R P_{R'} > e^{ik(R-R')} + c.c.$$ 

$$+ \frac{1}{v^2} \sum_{R, R'} |w_1(k)|^2 < P_R P_{R'} > e^{ik(R-R')}$$

$$+ |w_1'(-k)|^2 \sum_{R, R'} < (1 - P_R)(1 - P_{R'}) > e^{ik(R-R')} \right\} \right. , (2.39)$$

where $< \ldots >$ is the ensemble average.

If we assume that the correlation between rotating two inner hexagonal rings is Gaussian, the disorder is further specified by

$$< P_R > = \frac{1}{2}$$

$$< P_R P_{R'} > = \frac{1}{4} \left( e^{-\frac{(R-R')^2}{\alpha^2}} + 1 \right) . (2.40)$$

Using these properties of the random variables $P_R$, we have

$$< I(k) > = \frac{1}{v^2} \sum_{G} |w(G)|^2 \delta(k - G)$$
Using the relation

\[ \sum_{R,R'} e^{-\tfrac{(R-R')^2}{\Delta^2}} e^{i\mathbf{k} \cdot (R-R')} = N^2 \pi \frac{\Delta}{4} \sum_{G} e^{-\tfrac{(G)^2}{4\Delta^2}}. \]  

(2.42)

We have the final form of the diffraction intensity as

\[ < I(k) > = \frac{1}{v^2} \sum_{G} \left( |w(G)|^2 + \frac{1}{4} |w(G)^2 + |w'(G)|^2 \right) \]

\[ + \frac{1}{4} (w(G)w(-G) + c.c.) \]

\[ + \frac{1}{2} (w(G)(w(-G) + w'(G)) + c.c.) \delta(k - G) \]

\[ + \frac{1}{4} \pi \frac{\Delta}{2} (|w(k)|^2 + |w'(k)|^2 - (w(k)w'(k) + c.c.)) e^{-\tfrac{(G)^2}{4\Delta^2}} \}.

The resonance condition for bright spots in this diffraction is same as before. So, the pattern for the bright spot does not change. However, the diffraction peak shapes are changed. The peak shapes in this are the superpositions of \( \delta \)-functions with Gaussian shaped intensity distributions with maxima at the reciprocal lattice vectors \( G \). The peak widths are \( 2/\Delta \).

2.3.5 X-ray Powder Diffraction Patterns

X-ray powder diffraction experiments measure the diffraction intensities as a function of \( k \), where \( k \) is the magnitude of \( k \). No X-ray diffraction has been
performed on the dodecagonal phase. A theoretical X-ray powder diffraction pattern is shown in Figure 2.7. There is no disorder introduced in this calculation. All peaks have $\delta$-function peak shape.

A very interesting feature of the theoretical X-ray powder diffraction pattern is that large peaks always come as pairs in which two peaks are very close. As we shall see later in this chapter, this is a common feature of all pseudo-quasicrystals. It is a consequence of imperfect $n$-fold symmetry of the pseudo-quasicrystal. As we have shown in the early part of this section, the bright spots always come in as almost symmetry related pairs. In a X-ray powder diffraction where small grains of the sample are aligned in all directions, both peaks in a symmetry related pair show up in the powder diffraction pattern $I(k)$. The slight difference in the magnitudes of $G$ and $G'$ result in very close separation of the two peaks.

When disorder exist in pseudo-quasicrystals, the diffraction peaks have finite widths. If the peak widths are comparable to the separation $\Delta k$ of peaks in a pair, these pairs will merge into broader peaks with double-maxima. In the decagonal pseudo-quasicrystal, in addition to double maxima peaks, there are also multi-maxima peaks. In Figure 2.8, a double-maxima diffraction peak in the $I(k)$ is shown in finer scale. It results from the two bright peaks at $G = 7G_1$ and $G' = 4G_1 + 4G_2$. The center of these two peaks are separated by $\Delta k \equiv (\frac{14}{\sqrt{3}} - 8)\frac{2\pi}{(2 + \sqrt{3})\Lambda} \approx 0.072G_0$, where $G_0 \equiv |G_1| = |G_2|$. The shape of each peak follows the Gaussian distribution $e^{(\mathbf{k} - G)^2/\Gamma^2}$, where $\Gamma$ is chosen to be $0.04G_0$. This implies that the correlation length $\xi$ of trans-
Figure 2.7: The theoretical X-ray powder diffraction pattern $I(k)/I(0)$ of the dodecagonal pseudo-quasicrystal. $G_0 = 0.324\AA^{-1}$ for interatomic spacing $A = 6\AA$. 
Figure 2.8: A double-maxima diffraction peak in the theoretical X-ray powder diffraction pattern of the pseudo-quasicrystal with disorders.
lational order is $25\left(\frac{1}{\xi_0}\right)$. Using the experimental value of $A$ ($\sim 6\text{Å}$), we have $\xi \sim 10^2\text{Å}$.
2.4 The Octagonal Pseudo-quasicrystals

2.4.1 Model Structures

A model structure of the octagonal quasicrystal is a square lattice with a 14-atom basis. It is shown in Figure 2.9a. The primitive lattice vectors of the square lattice are

\[ \mathbf{a}_1 = (2 + \sqrt{2})\hat{x} \]
\[ \mathbf{a}_2 = (2 + \sqrt{2})\hat{y}. \]  

The Wigner-Seitz cell of the octagonal pseudo-quasicrystal is shown in Figure 2.9b. The locations of the atoms in a Wigner-Seitz cell are

\[ c_0 = 0 \]
\[ c_j = \cos\left(\frac{j\pi}{4}\right)\hat{x} + \sin\left(\frac{j\pi}{4}\right)\hat{y}, \quad j = 1, \ldots, 8 \]
\[ c_j = (2 + \sqrt{2})^{\frac{3}{2}}(\cos\left((j - \frac{15}{2})\frac{\pi}{4}\right)\hat{x} + \sin\left((j - \frac{15}{2})\frac{\pi}{4}\right)\hat{y}), \quad j = 9, \ldots, 16 \]
\[ c_j = (1 + 1/\sqrt{2})(\cos\left((j - \frac{31}{2})\frac{\pi}{2}\right)\hat{x} + \sin\left((j - \frac{31}{2})\frac{\pi}{2}\right)\hat{y}), \quad j = 17, \ldots, 20. \]

The four atoms at corners are shared by four cells. The eight atoms on the edges are shared by two cells. So, the total number of atoms in each unit cell is 14. We came up with structure partly from observing on of the high resolution electron micrograph of the octagonal phase and partly from the symmetry consideration.

We have another version of octagonal pseudo-quasicrystal which is a square lattice with a 28-atom basis. Its diffraction pattern is slightly closer
Figure 2.9: The Wigner-Seitz cell and a portion of the octagonal pseudo-quasicrystal. a) The Wigner-Seitz cell of the octagonal pseudo-quasicrystal. b) A portion of the octagonal pseudo-quasicrystal.
to a perfectly 8-fold one than that of the 14-atoms version. However, since we want to keep the unit cell of the crystal as small as possible while its diffraction resembles the experimental one, we shall discuss only the 14-atom version in detail.

2.4.2 Electron Diffraction Pattern

The density Fourier transform of the octagonal pseudo-quasicrystal can be calculated in a straightforward manner. It is given by

$$\rho(k) = \sum G \delta(k - G)w(G),$$  \hspace{1cm} (2.46)

where the reciprocal lattice vectors are

$$G = n_1 G_1 + n_2 G_2$$
$$= \frac{2\pi}{2 + \sqrt{2}} (n_1 \hat{x} + n_2 \hat{y}),$$  \hspace{1cm} (2.47)

and the structure factor is given by

$$w(G) = 1 + (-1)^{n_1+n_2} + 2e^{i\frac{2\pi}{\sqrt{2}}n_1} + 2e^{i\frac{2\pi}{\sqrt{2}}n_2}$$
$$+ (-1)^{n_1-n_2} e^{i\frac{2\pi}{\sqrt{2}}n_1} + (-1)^{n_1-n_2} e^{i\frac{2\pi}{\sqrt{2}}n_2}$$
$$+ (-1)^{n_1+n_2} e^{-i\frac{2\pi}{\sqrt{2}}n_1} + (-1)^{n_1+n_2} e^{-i\frac{2\pi}{\sqrt{2}}n_2}$$
$$+ 2(-1)^{n_1+n_2} \cos\left(\frac{2\pi}{\sqrt{2}}(n_1 + n_2)\right)$$
$$+ 2(-1)^{n_1-n_2} \cos\left(\frac{2\pi}{\sqrt{2}}(n_1 - n_2)\right).$$  \hspace{1cm} (2.48)

The diffraction pattern are given by $$I(k) = \sum G \delta(k - G)|w(G)|^2.$$ A full resolution diffraction pattern is shown in Figure 2.10. The periodicity of the
Figure 2.10: The theoretical full resolution diffraction pattern of the octagonal pseudo-quasicrystal. δ-function peaks are located at the centers of the circles. The radii are proportional to the diffraction intensities. For peaks with intensities less than .01I(0), the size of the circles are uniform.
square reciprocal lattice is obvious in this full resolution diffraction pattern. However, if the threshold is raised to 0.2I(0), the diffraction pattern looks almost 8-fold symmetric as shown in Figure 2.11. The exact symmetry of this pattern is still 4-fold. The reason why it looks almost 8-fold symmetric is exact same as in the dodecagonal pseudo-quasicrystal. This finite resolution diffraction pattern can account for most of diffraction spots in the experimental electron diffraction pattern[2]. However, there are bright diffraction spot in the experimental pattern can not be accounted by this theoretical pattern.

Figure 2.12 shows the superposition of the theoretical diffraction pattern in Figure 2.11 rotated by 2\pi/8 and itself. The purpose of this figure is twofold.

On one hand, the mismatches of the circles show the imperfect 8-fold symmetry of the finite resolution diffraction pattern. One can see that larger deviations show up in peaks with smaller intensities. Diffraction spots with large intensities appear almost perfectly 8-fold symmetric.

On the other hand, it also can be regarded as a diffraction pattern of a 45° twin of the octagonal pseudo-quasicrystals in which crystallites scatter in coherently. If the disorder in each crystallite broaden diffraction peaks from \delta-function to peaks with finite widths, the shapes of the diffraction spots are elongated along certain directions as indicated by Figure 2.12.

The agreement of the theoretical and the experimental diffraction spot shapes is not very good. These elongated diffraction spot shapes agree with some observed diffraction spot shapes. However, there are large diffraction
Figure 2.11: The theoretical finite resolution diffraction pattern of the octagonal pseudo-quasicrystal. Only peaks with intensity larger than $0.2I(0)$ are shown. $\delta$-function peaks are located at the centers of the circles. The radii are proportional to the diffraction intensities.
Figure 2.12: An illustration of the imperfect 8-fold symmetry of the diffraction pattern in Figure 2.11. Mismatches of the circles show the imperfectness of the symmetry. Only peaks with intensity larger than 0.2$I(0)$ are shown. $\delta$-function peaks are located at the centers of the circles. The radii are proportional to the diffraction intensities.
spots with triangular shape in the experimental diffraction pattern[2]. It is not clear how these triangular diffraction spot shapes can be explained by the twinning of the octagonal pseudo-quasicrystal model.

2.4.3 Why are the Finite Resolution Diffraction Pattern So 8-fold Symmetric?

The pseudo-octagonal symmetry of the electron diffraction pattern of the octagonal pseudo-quasicrystal can be quantitatively understood as follows.

The bright diffraction spots occur when all terms in Eq.(2.48) are "resonance". From the Eq.(2.48), we find the resonance condition for bright peaks in diffraction pattern of the octagonal pseudo-quasicrystal:

Both \( n_1 \) and \( n_2 \) have the same parity and satisfy the following equations

\[
\begin{align*}
\frac{1}{\sqrt{2}}n_1 &= m_1 + \epsilon_1 \\
\frac{1}{\sqrt{2}}n_2 &= m_2 + \epsilon_2,
\end{align*}
\]

(2.49)

where \( m_1 \) and \( m_2 \) are integers with the same parities, and \( \epsilon_1, \epsilon_2 \ll 1 \).

For any reciprocal lattice vector \( \mathbf{G} = n_1 \mathbf{G}_1 + n_2 \mathbf{G}_2 \), after a \( 2\pi/8 \) rotation about the z-axis, we have

\[
\mathbf{G} \rightarrow \mathbf{k}' = \frac{n_1 - n_2}{\sqrt{2}} \mathbf{G}_1 + \frac{n_1 + n_2}{\sqrt{2}} \mathbf{G}_2,
\]

(2.50)

where \( \mathbf{k}' \) is not a reciprocal lattice vector. However, for every bright spot satisfying the resonance condition, \( \mathbf{k}' \) can be rewritten as

\[
\begin{align*}
\mathbf{k}' &= (m_1 - m_2) \mathbf{G}_1 + (m_1 + m_2) \mathbf{G}_2 \\
&\quad + (\epsilon_1 - \epsilon_2) \mathbf{G}_1 + (\epsilon_1 + \epsilon_2) \mathbf{G}_2.
\end{align*}
\]

(2.51)
So, the reciprocal lattice vector \( G' = (m_1 - m_2)G_1 + (m_1 + m_2)G_2 \) is very close to \( k' \), because all \( \varepsilon \)'s are very small.

The intensity of the peak at \( G' \) is given by \( I(G') = |w(G')|^2 \), where the structure factor \( w(G') \) is

\[
\begin{align*}
w(G') & = 2 + 2\cos(2\pi \sqrt{2} \varepsilon_1) + 2\cos(2\pi \sqrt{2} \varepsilon_2) \\
& + 3e^{-i\frac{\pi}{2} (\varepsilon_1 - \varepsilon_2)} + 3e^{-i\frac{\pi}{2} (\varepsilon_1 + \varepsilon_2)} \\
& + e^{i\frac{\pi}{2} (\varepsilon_1 - \varepsilon_2)} + e^{i\frac{\pi}{2} (\varepsilon_1 + \varepsilon_2)}. \quad (2.52)
\end{align*}
\]

Eq.(2.49) and the property of \( n_1 \) and \( n_2 \) having the same parity have been used to obtain this expression. Since all \( \varepsilon \)'s are very small, the intensity of the peak at \( G' \) is also large. Thus, we have proved the theoretical electron diffraction pattern have almost perfect 8-fold symmetry.

### 2.4.4 X-ray Powder Diffraction

Similar to the X-ray powder diffraction pattern of the dodecagonal pseudo-quasicrystal, strong diffraction peaks occur in pairs in the diffraction pattern \( I(k) \). A theoretical X-ray powder diffraction pattern \( I(k) \) vs. \( k \) is shown in Figure 2.13. If disorder are introduced into the octagonal pseudo-quasicrystal, the diffraction peak will be broadened. These \( \delta \)-function doublets in the diffraction pattern will become double-maxima peaks. Due to the nature of the disorder in the octagonal pseudo-quasicrystal is not clear, we shall not discuss this in any more detail.
Figure 2.13: The theoretical X-ray powder diffraction pattern \( I(k)/I(0) \) of the octagonal pseudo-quasicrystal. \( G_0 = 0.307\,\text{Å}^{-1} \) for the interatomic spacing \( A = 6\,\text{Å} \).
2.5 The Decagonal Pseudo-quasicrystal

As we mentioned in section 2.1, quasicrystal model is not suitable to explain many observed features of the decagonal phase. The two major criticisms against the decagonal quasicrystal model are: 1) the distribution of diffraction intensities of the calculated diffraction pattern of the decagonal quasicrystal[1] is significantly different from the experimental one; 2) it seems that it is very difficult to explain the multi-maxima diffraction peaks observed in the X-ray powder diffraction experiments[9,10].

In this section, we shall discuss the decagonal pseudo-quasicrystal which can overcome the difficulties mentioned above. As we shall see, its distribution of diffraction densities agrees with the experimental one much better than that of a decagonal quasicrystal does. There are also double- and multi-maxima peaks in the calculated X-ray powder diffraction pattern of $I(k)$.

2.5.1 Model Structures

A large portion of decagonal pseudo-quasicrystal and the Wigner-Seitz cell of its crystal structure are shown in Figure 2.14. This crystal structure is obtained by translating the Wigner-Seitz cell through all integral linear combinations of the two primitive lattice vectors:

$$a_1 = [(2 + 3c_1 + c_2)\hat{x} - (s_1 + s_2)\hat{y}]\AA,$$

$$a_2 = [(2 + 3c_1 + c_2)\hat{x} + (s_1 + s_2)\hat{y}]\AA,$$  (2.53)
Figure 2.14: The Wigner-Seitz cell and a portion of the decagonal pseudo-quasicrystal.  

(a) The Wigner-Seitz cell of the decagonal pseudo-quasicrystal.  
(b) A portion of the decagonal pseudo-quasicrystal.
where \( c_1 = \cos 36^\circ, s_1 = \sin 36^\circ, c_2 = \cos 72^\circ, s_2 = \sin 72^\circ; \) and \( A \) is the length of the atomic bond. There are 18 base atoms in each unit cell whose locations are:

\[
0, \\
A(\cos\left(\frac{j - \frac{1}{2}}{5}\right)2\pi)\hat{x} + \sin\left(\frac{j - \frac{1}{2}}{5}\right)2\pi)\hat{y}, \quad j = 0, \ldots, 4 \\
2c_1 A(\cos\left(\frac{j - 1}{5}\right)\pi)\hat{x} + \sin\left(\frac{j - 1}{5}\right)\pi)\hat{y}, \quad j = 0, \ldots, 7 \\
A(1 + 2c_1)\hat{x}, \quad -A(2 + 2c_2)\hat{x} \\
A(3c_1 \hat{x} + s_1 \hat{y}), \quad A(3c_1 \hat{x} - s_1 \hat{y}),
\]

(2.54)

There are many small decagons in the decagonal pseudo-quasicrystal. Inside each decagon, there is a pentagonal star. There many ways to construct crystal structures with these decagons. The present structure was established mostly from symmetry consideration. This structure gives the diffraction pattern closest to the 10-fold symmetric one while the number of atoms per unit cell is small.

2.5.2 Electron Diffraction Pattern

A full resolution theoretical electron diffraction pattern is shown in Figure 2.15. The two primitives of the reciprocal lattice are:

\[
G_1 = \left[\frac{1}{2(2 + 3c_1 + c_2)}\hat{x} - \frac{1}{2(s_1 + s_2)}\hat{y}\right]2\pi A \\
G_2 = \frac{1}{2(2 + 3c_1 + c_2)}\hat{x} + \frac{1}{2(s_1 + s_2)}\hat{y}\frac{2\pi}{A},
\]

(2.55)
Figure 2.15: The theoretical full resolution diffraction pattern of the decagonal pseudo-quasicrystal. $\delta$-function peaks are located at the centers of the circles. The radii are proportional to the diffraction intensities. For peaks with intensities less than $0.01I(0)$, the size of the circles are uniform.
The diffraction intensity $I(k)$ is given by

$$I(k) = \sum_{G} \delta(k - G) |W(G)|^2,$$

(2.56)

where the structure factor is

$$W(G) = \sum_{j=1}^{18} e^{iG \cdot c_j},$$

(2.57)

where $\{c_j\}$ are the positions of the base atoms in a unit cell listed above.

The rhombic reciprocal lattice is apparent in the full resolution diffraction pattern. However, the diffraction pattern becomes almost 10-fold symmetric when the threshold is raised to $0.25 I(0)$ as shown in Figure 2.16. Comparing, this finite resolution diffraction pattern and the experimental electron diffraction pattern [9] shows excellent agreement. The finite resolution diffraction pattern of a decagonal quasicrystal agrees with that of the decagonal phase very well, except the square shape of the diffraction shapes.

The decagonal pseudo-quasicrystal have many local degeneracies like the local phason degeneracies (i.e. flipping tiles) in quasicrystals. The bond orientational symmetry is preserved during flipping tiles. There are other local degeneracies. For example, rotating the pentagonal star in the Wigner-Seitz cell by $2\pi/10$ introduce neither new tiles nor mismatches of tiles. Randomly distributing these local degenerate configuration creates disorder in the decagonal pseudo-quasicrystal. These disorder broaden the $\delta$-function shape diffraction peaks into peaks with finite widths.

Next, consider a 5-fold multiple twinning of the decagonal pseudo-quasicrystals. Assuming the diffractions form different crystallite are not coherent, the elec-
Figure 2.16: The theoretical finite resolution diffraction pattern of the decagonal pseudo-quasicrystal. Only peaks with intensity larger than $0.2I(0)$ are shown. $\delta$-function peaks are located at the centers of the circles. The radii are proportional to the diffraction intensities.
tron diffraction of the multiple twinning is the incoherent superposition of
diffraction form each crystallites. A theoretical electron diffraction pattern
of a such multiple twinning is in Figure 2.17. Due to the imperfect 10-fold
symmetry, each spot in the diffraction pattern of the multiple twinning of
the pseudo-quasicrystals is composed of five separated spots. The disorder
smears out the δ-function peaks. The shape of each resulting peak is
determined by the incoherent superposition of these five individual spots.
It turns out that these shapes are triangles oriented in certain directions.
Although this is just two-dimensional, we notice that it agrees with the 5-
fold electron diffraction pattern of the AlCrRu icosahedral phase[11]. These
spots shapes and their orientations match perfectly over the entire observ-
able k-space. Currently, these triangular shapes are also explained in terms
of phason strains[12]. The shape of a particular diffraction spot is calculated
in a rather complicated method. The result of Ref. 12 account for the exper-
imental observation well. To comparison, we feel our explanation simpler.

However, the shapes of the diffraction spots of the decagonal phase are
squares[9]. We have yet not found a crystal structure which gives square
diffraction spots. On the other hand, we have studied only a limited number
of decagonal pseudo-quasicrystals. It is entirely conceivable that the square
spot shapes can be accounted within the pseudo-quasicrystal model.
Figure 2.17: An illustration of the imperfect 10-fold symmetry of the diffraction pattern in Figure 2.16. Mismatches of the circles show the imperfectness of the symmetry. Only peaks with intensity larger than $0.2I(0)$ are shown. δ-function peaks are located at the centers of the circles. The radii are proportional to the diffraction intensities.
2.5.3 X-ray Powder Diffraction Pattern

A theoretical X-ray powder diffraction pattern \( I(k) \) is shown in Figure 2.18. It is interesting to note that diffraction peaks with large intensities occur in clusters. Some clusters have two strong peaks, and some have three or even four strong diffraction peaks. The separations of these peaks in different clusters are very different. Usually, the separations are smaller for peaks with larger intensities. For those very intense peaks, the separations are so small that they hardly resolve in Figure 2.18. This is the consequence of the imperfect 10-fold symmetry of the decagonal pseudo-quasicrystal.

In the presence of disorder in the decagonal pseudo-quasicrystal, the diffraction peaks will be broadened. When the peak widths are comparable to the separation of peaks in a cluster, these peaks will merge into a multi-maxima peak. The resulting peak width is proportional to the separation between the original peaks. This explains why the peak widths of the more intense peaks are smaller, as they are more closely spaced. This special peak width dependence has also been recently explained in terms of phason strain (See discussion in section 1.2). However, our explanation can further explain the multi-maxima peaks in the X-ray powder diffraction. From the electron micrograph, we find the atomic space \( A \) is about 6\( \text{Å} \). Consequently, the separation between intense peaks in clusters range from comparable to much less than 0.01\( \text{Å}^{-1} \). In high resolution X-ray experiment, the solution is 0.01\( \text{Å}^{-1} \). This might explain why there are clusters of X-ray powder diffraction peaks which are not resolvable. Neither double-maxima peaks in the
Figure 2.18: The theoretical X-ray powder diffraction pattern of a decagonal pseudo-quasicrystal. $G_0 = 0.35\text{Å}^{-1}$ for the interatomic spacing $A = 6\text{Å}$. 
icosahedral phase nor multi-maxima peaks in the decagonal phase have been explained in terms of phason strains. The phason strains proposed in Ref. 11 might be able to explain the double-maximal peak in the icosahedral phase. There are three regions in a triangular diffraction spot having peak intensities. According to their calculation, the k's of the centers of two of these three regions have the same magnitude. Therefore, in a X-ray powder diffraction this triangular diffraction spot results in a double-maxima peak.

In this chapter, we have proposed a 1D and 2D examples to show that within a wide range of the resolution of diffraction intensities and positions of diffraction spots the diffraction pattern of some crystal with incommensurate bases are indistinguishable from those of the quasicrystals. In particular, the diffraction patterns of the dodecagonal and the decagonal pseudo-quasicrystals account the observed electron diffraction patterns of the dodecagonal and the decagonal phase very well. The 1D resonance and its 2D analogue play the most important roles in these phenomena. Multiple twinnings of these pseudo-quasicrystals are needed only in the explanation of the diffraction spot shapes in the electron diffraction pattern and the multi-maxima peaks in the X-ray powder diffraction patterns. The symmetries of the diffraction patterns of these n-fold pseudo-quasicrystals can be even closer to the perfect n-fold symmetries (n=8,10,12) if some particular sets of the atomic form factors are used in the calculation of the diffraction patterns.
2.5.4 Super Rational Approximates of the Decagonal Perfect Quasicrystal

The rational approximates of the decagonal perfect quasicrystal have been discussed in the Ref. 13. In the paper, a construction scheme of the rational approximates of the decagonal perfect quasicrystal has been given. The discussions there have been focused on the real space structures instead of the diffraction patterns of the rational approximates.

It turns out that their scheme can generate crystal structures which are very similar to our decagonal pseudo-quasicrystal. Some of the rational approximates differ from the decagonal pseudo-quasicrystal only by periodically flipping a set of tiles. The Bravais lattices of these crystal structures are same as that of the decagonal pseudo-quasicrystal. One of the diffractions pattern of these rational approximates is almost indistinguishable from that of the decagonal pseudo-quasicrystal.

Before further discussions of the properties of these rational approximates, we first briefly review the construction scheme given in the Ref. 13. These rational approximates are obtained by projecting the lattice points inside a rational strip of the $5D$ cubic lattice onto a $2D$ irrational physical space which is the same as that in the decagonal perfect quasicrystal. In our language, they are super rational approximates. The rational strip is defined as follows.

First, choose a $2D$ rational hyperplane $P_{pq}$ perpendicular to the $(11111)$ direction in the $5D$ space. The purpose of this choice is to minimize the difference between the real space structures of the rational approximates
and those of the quasicrystals. This 2D rational hyperplane is chosen to be parallel to a lattice plane determined by two 5D lattice vectors \( \mathbf{p} = (p_0, p_1, p_2, p_3, p_4) \) and \( \mathbf{q} = (q_0, q_1, q_2, q_3, q_4) \), with \( \sum_{i=0}^{4} p_i = 0 \) and \( \sum_{i=0}^{4} q_i = 0 \).

Then, a perpendicular space \( P_{pq}^\perp \) is defined to be a 3D subspace orthogonal to the rational hyperplane \( P \) in the 5D space. Denote \( C_\perp \) as the projection of a 5D cubic unit cell onto the \( P_{pq}^\perp \). The rational strip is defined as \( C_\perp \oplus P_{pq} \).

Besides the perpendicular space \( P_{pq}^\perp \) determined by the rational hyperplane \( P_{pq} \), there is another 3D perpendicular space \( P_{irr}^\perp \) which is orthogonal to the irrational physical space. This is the original perpendicular space in the construction of the perfect quasicrystal. The difference between the rational approximate and the decagonal perfect quasicrystal can be measured by the projections of the lattice vectors \( \mathbf{p} \) and \( \mathbf{q} \) on to the perpendicular space \( P_{irr}^\perp \). The smaller these projections, the closer the real space structure of a rational approximate to that of the decagonal quasicrystal.

Next, choose the basis vector of the perpendicular space \( P_{irr}^\perp \) as

\[
\hat{u}_1 = \sqrt{\frac{2}{5}} \sum_{i=0}^{4} \cos \frac{4\pi i}{5} \hat{e}_i, \quad \hat{u}_2 = \sqrt{\frac{2}{5}} \sum_{i=0}^{4} \sin \frac{4\pi i}{5} \hat{e}_i, \quad \hat{u}_3 = \frac{1}{\sqrt{5}} \sum_{i=0}^{4} \hat{e}_i, \quad (2.58)
\]

where \( \{\hat{e}_i\} \) are the basis vectors of the 5D cubic lattice. The projection of \( \mathbf{p} \) onto the \( P_{irr}^\perp \) is

\[
\tilde{\mathbf{p}} = \sum_{i=0}^{4} \tilde{p}_i \hat{e}_i, \quad (2.59)
\]

where

\[
\tilde{p}_i = \frac{2}{5} \sum_{j=0}^{4} p_j \cos \frac{4\pi(j - i)}{5}. \quad (2.60)
\]
The property of $P_{pq}$ perpendicular to $u_3$ has been used in this derivation. From the Eq.(2.60), one can find that

$$\hat{p}_{i+1} + \hat{p}_{i-1} = \hat{p}_i. \tag{2.61}$$

Using the recursion relation Eq.(2.61), one can express the $\hat{p}$ in terms of $\hat{p}_1$ and $\hat{p}_2$ as the following

$$\hat{p} = (-\tau \hat{p}_1 - \hat{p}_2, \hat{p}_1, -\tau \hat{p}_2 - \hat{p}_1, \tau \hat{p}_1 + \tau \hat{p}_2), \tag{2.62}$$

where

$$\hat{p}_1 = \frac{1}{\sqrt{5}}(\tau p_1 + p_3 + p_4),$$

$$\hat{p}_1 = \frac{1}{\sqrt{5}}(p_2/\tau - p_1 - p_3). \tag{2.63}$$

The result of the elementary number theory shows that the best sequence to approach $1/\tau$ is \{f_m/f_{m+1}, m = 0, 1, 2, \} where $f_m$ and $f_{m+1}$ are the $m^{th}$ and the $(m + 1)^{th}$ Fibonacci numbers. To minimize the projection of $p$ onto the $P_{trr}^\perp$, we choose

$$p_1 = -(p_3 + p_4)f_m, \quad f_{m+1},$$

$$p_2 = (p_1 + p_3)f_{i+1}f_i. \tag{2.64}$$

Similar argument can be applied to $q$. Combining these result, we can choose[13]

$$p = (0, f_{p+1}, f_p, -f_p, -f_{p+1}),$$

$$q = (-f_{q+1}, 0, f_{q+1}, f_q, -f_q). \tag{2.65}$$
or

\[ p = (0, f_{p+1}, f_p, -f_p, -f_{p+1}), \]
\[ q = (-f_q, -f_{q+1}, 0, f_{q+1}, f_q). \]  
(2.66)

The first choice gives a super rational approximate with a 72° rhombic unit cell (so-called fat rhombus). The second choice gives a super rational approximate with a 36° rhombic unit cell (so-called thin rhombus). We define the order of the rational approximate within this family of rational approximates, where the order is defined as \((p, q)\). The order only uniquely determine the Bravais lattice and the number of atoms per unit cell. Different decorations of the unit cell can be obtained by shifting the rational strip along the perpendicular plane \(P^\bot\).

Figure 2.19 shows a \((2,2)\) order super rational approximate constructed by the above scheme. In this construction, \(p\) and \(q\) have been chosen as

\[ p = (0, 2, 1, -1, -2), \]
\[ q = (-1, -2, 0, 2, 1). \]  
(2.67)

It is easy to find that the Wigner-Seitz cell of this super rational approximate differs from that of the decagonal pseudo-quasicrystal only by rotating the inner pentagonal star by \(2\pi/10\). The Bravais lattices of these two crystal structures are exactly same. The similarity between the diffraction pattern of this \((2,2)\) order super rational approximate and that of the decagonal pseudo-quasicrystal is shown as follows.
Figure 2.19: The Wigner-Seitz cell and a portion of the $(2,2)^{th}$ super rational approximant. a) The Wigner-Seitz cell of the super rational approximant of the decagonal perfect quasicrystal. b) A portion of the crystal lattice structure of the super rational approximant.
The diffraction pattern of the (2,2) order super rational approximate is given by the distribution of diffraction intensities:

\[
I(k) = \sum_{\mathbf{G}} \delta(k - \mathbf{G})|W(\mathbf{G})|^2
\]

\[
= \sum_{\mathbf{G}} \delta(k - \mathbf{G})|w_1(\mathbf{G}) + w_2(\mathbf{G}) + w_3(\mathbf{G})|^2, \tag{2.68}
\]

where the structure factor \(W(\mathbf{G})\) has been decomposed into three parts. \(w_1(\mathbf{G})\) is the contribution of the five atoms \(\{c_j^{(1)}, j = 1, \ldots, 5\}\) nearest to the center. \(w_2(\mathbf{G})\) is the contribution of the four atoms \(\{c_j^{(2)}, j = 1, \ldots, 4\}\) on the four short edges of the Wigner-Seitz cell. \(w_3(\mathbf{G})\) is the contribution from the rest of atoms \(\{c_j^{(3)}, j = 1, \ldots, 17\}\) in the Wigner-Seitz cell. The inversion symmetry of this group of atoms implies that \(w_3(-\mathbf{G}) = w_3(\mathbf{G})\).

On the other hand, the diffraction pattern of the decagonal pseudo-crystal is determined by a distribution of diffraction intensities of the form similar to Eq.(2.68), i.e.

\[
I'(k) = \sum_{\mathbf{G}} \delta(k - \mathbf{G})|W'(\mathbf{G})|^2
\]

\[
= \sum_{\mathbf{G}} \delta(k - \mathbf{G})|w'_1(\mathbf{G}) + w'_2(\mathbf{G}) + w'_3(\mathbf{G})|^2, \tag{2.69}
\]

where \(w'_1(\mathbf{G})\) have the same interpretations as above except that the locations of the five atoms \(\{c_j, j = 1, \ldots, 5\}\) nearest to the center are different. The superscript "r" means decagonal pseudo-quasicrystal. Comparing Figure 2.14a with Figure 2.19a shows that

\[
w'_1(\mathbf{G}) = w_1(-\mathbf{G}),
\]

\[
w'_2(\mathbf{G}) = w_2(\mathbf{G}),
\]
\[ w'_3(G) = w_3(G). \quad (2.70) \]

Since the two Bravais lattice are exactly same, the reciprocal lattice vectors are in Eq.(2.68) and Eq.(2.69) are same. Therefore, one only needs to compare the intensities for the peaks with the same \( G \) in two patterns. Using the Eq.(2.68), Eq.(2.69) and Eq.(2.70), we find that the difference in the intensities is

\[ \Delta I(G) \equiv I(G) - I'(G) \]
\[ = w_1(G)w_2(-G) + w_1(-G)w_2(G) \]
\[ - w_1(-G)w_2(-G) - w_1(G)w_2(G) \]
\[ = 4\text{Re}w_2(G)\text{Im}w_1(-G). \quad (2.71) \]

The condition for having maximal difference in diffraction intensities is

\[ G \cdot c_i^{(1)} = \pi(2m_i + 1) + \epsilon_i, \quad i = 1, \ldots, 4 \]
\[ G \cdot c_j^{(2)} = 2\pi n_j + \epsilon_j, \quad j = 1, \ldots, 5, \quad (2.72) \]

where \( m_i \) and \( n_j \) are integers, and \( |\epsilon_{i,j}| \ll 1 \). The Eq.(2.71) shows that the upper bound of the \( \Delta I(G)/I(0) \) is \( 40/18^2 \approx 0.12 \).

Since we have chosen the location of the central atom to be zero, the resonance condition is

\[ G \cdot c_j^{(i)} = 2\pi m_j^{(i)} + \delta_j^{(i)}, \quad (2.73) \]

where \( |\delta_j^{(i)}| \ll 1 \). It is clear that the resonance condition Eq.(2.73) and the condition Eq.(2.72) for maximal difference in diffraction intensities can never
be satisfied simultaneously. Therefore, the large differences can only appear in weak diffraction spots. Of course, these large differences are smaller than the upper bound 0.12I(0).

Although the upper bound of the difference in intensities is small, the numerical solution shows the real maximal difference in the intensities is even smaller. We have superimposed the full resolution diffraction patterns of the (2,2) super rational approximate and the decagonal pseudo-quasicrystal. There is no human eye detectable difference showing up in this superposition of the two diffraction patterns. This fact indicates that the maximal difference in the intensities of the two diffraction patterns is about .02I(0) which is about 1/6 of the upper bound given above.

As we have mentioned above, shifting the rational strip along the perpendicular space $P^\perp$ results in different decorations of the unit cell. We have not yet found the shifting of the rational strip such that the resulting super rational approximate has the exactly same real space structure of the decagonal pseudo-quasicrystal. Nevertheless, we believe that the decagonal pseudo-quasicrystal is one of the (2,2) order super rational approximates.
References


CHAPTER III

Faceting in Quasicrystals and Perfect Bond Oriented Glasses

3.1 Introduction

As we mentioned in section 1.1.4, the recently discovered icosahedral phases of Al₆Li₃Cu and GaMgZn have two remarkable features. On one hand, they have large faceted dendrite tips. The shapes of the tips of the growth dendrites of the Al₆Li₃Cu and GaMgZn icosahedral phase are triacontahedral and dodecahedral respectively. (See Figure 3.1 and Figure 3.2 for the geometrical shapes of these polyhedra).

The sizes of the facets range from 0.1mm to 2cm. On the other hand, X-ray experiments show that the diffraction peaks of Al₆Li₃Cu have "intrinsic" widths quantitatively similar to those observed in the rapidly quenched icosahedral phases. These finite peak widths indicate the correlation lengths are of the order of 200Å to 1000Å, which are several orders of magnitude shorter than the sizes of the facets.
Figure 3.1: A triacontahedron.
Figure 3.2: A dodecahedron.
The coexistence of the large facets and substantial amount of disorder raises a conceptual question. Usually, facets are thought to be the consequences of the long range translational order[1]. (An infinite long range translational order implies that the density Fourier transform is a set of δ-functions). If this is the case, the sizes of the facets should be comparable to the correlation length. The experiments contradict this expectation. The experimental observations suggest that the long range translational order may be only a sufficient condition but not a necessary one for faceting in equilibrium shapes.

A noticeable property of the icosahedral phase Al₈Li₃Cu and GaMgZn is that they can be obtained via slowly cooling processes. This indicates that they may in fact be thermodynamically stable phases.

Although the cooling rate is $10^6$ slower than that in the rapidly quenching, it is still very fast. As a result, these quasicrystal phases may not grow in completely equilibrium processes as indicated by the growth dendrites. So, the experiments have only shown that disorder can be compatible with faceted growth (rather than equilibrium) shapes. Nevertheless, the growth shapes are related to the $T = 0$ equilibrium shapes as we shall see later in this chapter.

To understand the compatibility of large growth facets and disorder, we shall address the following questions[2]: whether a disordered system can have equilibrium facets? What is the origin of the facet formation?

The decagonal phase has higher degrees of disorder. No large grain of
the decagonal phase has been obtained yet. Consequently, there is almost no experimental study on the facets of the decagonal phase. For this reason, I shall not discuss the faceting phenomenon in the decagonal phase.

Roughening transition is a very interesting aspect of the faceting phenomenon. The current understanding of the roughening transition in quasicrystals has been summarized in section 1.2.4. So, it will not be discussed here.
3.2 The Determination of the Equilibrium Shapes of Solids

In this section, we shall briefly review the well known Wulff construction. A new computational algorithm for applying the Wulff construction will be discussed in detail.

The $T = 0$ equilibrium shape of a solid is determined by minimizing the total surface energy subject to the constraint of constant volume. We have assumed the bulk of the solid to be in equilibrium. We let $\gamma(\hat{n})$ be the surface energy density of a macroscopic flat surface of the average normal $\hat{n}$. The extremum condition is then written as

$$\delta \int_{\Sigma} ds (\gamma(\hat{n}) - \lambda \hat{n} \cdot r) = 0, \quad (3.1)$$

where $\hat{n}$ is the normal of the surface at point $r$ on the surface $\Sigma$, and $\lambda$ is a Lagrange multiplier.

Wulff has shown[4] that the equilibrium shape implied by the Eq.(3.1) can be constructed by the following algorithm (the Wulff construction). First, construct a “polar-plot” of the surface energy density in which $\gamma(\hat{n})$ is represented by a radial vector along $\hat{n}$ with length $\gamma(n)$. $\hat{n}$ runs over all directions. Then, at each point of the polar-plot, construct a plane (or line in 2D) normal to the radial vector. The shape of the common interior bounded by these planes (or lines in 2D) is the equilibrium shape of the solid.

In many model calculations of the equilibrium shapes of solids, the surface energies usually are of the simple form of $\gamma(\hat{n}) = \sum_{\mu} g^{(\mu)} \sum_{\alpha} | A_{\alpha}^{(\mu)} \cdot \hat{n} |$. This
is a very general form which covers a large number of classes of solids such as simple crystals, perfect quasicrystals and even the bond oriented glasses (defined later in this chapter).

Utilizing the simplicity of this form of surface energies, we construct an efficient computational algorithm to determine the shape of solids. We shall start with this algorithm in $2D$, then generate it to $3D$.

We first represent all $\mathbf{n}$'s in $2D$ by a unit circle. Each point on the unit circle represents a direction parallel to the radial vector from the origin to this point. The unit circle is then divided into angular regions by the intersections of the unit circle with the lines $\mathbf{r} \cdot \mathbf{A}_\alpha^{(\mu)} = 0$. Within each angular region, the surface energy density can be rewritten as

$$\gamma(\mathbf{n}) = \{ \sum_\mu g^{(\mu)} \sum_\alpha \epsilon^{(\mu)}_{am} \mathbf{A}_\alpha^{(\mu)} \} \cdot \mathbf{n} = \mathbf{D}_m \cdot \mathbf{n}, \quad (3.2)$$

where $m$ is the label of the angular region, $\epsilon^{(\mu)}_{am} = +1$ or $-1$ depending on which side of the line $\mathbf{r} \cdot \mathbf{A}_\alpha^{(\mu)} = 0$ the angular region is on. Finally, the equilibrium shape of the $2D$ solid is the convex polygon of which the vertices are $\mathbf{D}_m$'s.

The equivalence of this algorithm to the Wulff construction is shown as following.

From Eq.(3.2), we note that in each angular region the polar-plot of the surface energy density is an arc of a circle centered at $\mathbf{D}_m/2$ and with diameter $|\mathbf{D}_m|$. Every circle passes the origin.
Consider three adjacent angular regions labeled by \((m - 1), m\) and \((m + 1)\). (See Figure 3.3). \(D_{m-1}, D_m\) and \(D_{m+1}\) are the three diameter vectors and also the vertices of the equilibrium shape. Edges are the line segments connecting \(D_{m-1}\) to \(D_m\) and \(D_m\) to \(D_{m+1}\). From the elementary geometry of the circle, we know that the line segment connecting \(D_{m-1}\) and \(D_m\) passes the intersection \(I_m\) of two adjacent circles and is perpendicular to line \(OI_m\). Therefore, it is also a line constructed in the Wulff construction. It is same for the line segment connecting \(D_m\) and \(D_{m+1}\). Any other line, constructed in the Wulff construction, passing an arbitrary point on the arc \(I_mI_{m+1}\) intersects the above two lines at \(D_m\). The rest of the line is on the outside of the two line segments connecting \(D_{m-1}\) to \(D_{m+1}\) and \(D_m\) to \(D_{m+1}\). Repeating this on all angular regions, the common interior bounded by the lines in the Wulff construction is identical to the interior of the polygon constructed by the new algorithm.

In 3D case, all directions are represented by a unit sphere. A set of planes given by \(r \cdot A_{\alpha}^{(\mu)} = 0\) intersect the unit sphere on great circles. These great circles divided the unit sphere into angular zones. Within each angular zone, signs of \(A_{\alpha}^{(\mu)} \cdot \hat{n}\) are fixed. So, the surface energy density can be rewritten as

\[
\gamma(\hat{n}) = \left\{ \sum_{\mu} g^{(\mu)} \sum_{\alpha} \epsilon_{\alpha m}^{(\mu)} A_{\alpha}^{(\mu)} \right\} \cdot \hat{n} \\
\equiv D_m \cdot \hat{n},
\]

where \(m\) is the label of the angular zone, \(\epsilon_{\alpha m}^{(\mu)} = +1\) or \(-1\) depending on which side of the plane \(r \cdot A_{\alpha}^{(\mu)} = 0\) the angular zone is on. The polar-plot of the surface energy density is a portion of a spherical surface centered at \(D_m/2\).
Figure 3.3: A schematic proof of the algorithm of determining the $T = 0$ equilibrium shape.
with diameter $|D_m|$. The equilibrium shape is a convex polyhedron of which vertices are the diameter vectors $D_m$'s. The facets are convex polygons. The edges are the line segments connecting the diameter vectors belong to angular zones sharing common arcs of the great circles. Similarly, it can be proved that this $3D$ algorithm is identical to the Wulff construction in $3D$.

From the Wulff construction, it is easily to find that cusps in the polar-plot of the surface energy density lead to facets in the equilibrium shape. Usually, the deeper the cusp, the larger the facet.
3.3 Re-examination of the Origin of Faceting Phenomenon

3.3.1 Long Range Translational Order and Facet Formation

In a crystal, the lattice planes are the consequences of the long range translational order. A faceted equilibrium shape reflects that certain planes are easier to form than others. From this one might conclude that facet is a sign of long range translational order.

In a perfect quasicrystal, there is a long range quasiperiodic translational order. It leads to quasiperiodically separated plane-like surfaces. It is very natural to expect that the $T = 0$ equilibrium shape is faceted because some of these plane-like surfaces are energetically more favorable than the others. One again attempts to conclude that these facets are signs of the long range translational order.

However, experiments have shown that long range translational order and large facets do not simultaneously occur in icosahedral phase Al$_6$Li$_3$Cu. Instead, the sizes of facets are 2 to 3 orders of magnitude longer than the correlation length of the translational order. This seems to be contradictory to the common expectations. The problem of such expectations is the implicit assumption that the plane-like surfaces also imply long range translational order. It turns out not to be true. The long range translational order simply means that the plane-like surfaces are correlated over a long range. Its absence (or finite peak widths in X-ray experiments) does not imply the absence
of these plane-like surfaces. It only indicates that the plane-like surfaces are uncorrelated beyond the scale of the short correlation length. In section 3.6, we shall construct the so called “quasiglasses” as examples in which separations of the plane-like structures are randomly distributed. However, the $T = 0$ shapes of the quasiglasses are completely faceted.

### 3.3.2 Cusps in Surface Energy Densities

As we have seen, cusps in the polar-plot of surface energy densities lead to facets in equilibrium shapes. It was pointed by Landau[6] that the surface energy densities of crystals usually have “linear” cusps. The origins of these cusps are the “steps” on the crystal surfaces.

Consider a simple square crystal where the atoms interact with nearest neighbor interactions. The surface energy density is proportional to the number of bonds cut per unit area of the surface. Let plane $P$ be an equilibrium surface which has the lowest surface energy density. Plane $P'$ is another plane tilted from this by a small angle $\theta$. The microscopic structure of the plane $P'$ is a sequence of steps. Each of these steps is a segment of plane parallel to the plane $P'$. Each step creates an extra horizontal dangling bond. Therefore, the plane $P'$ has a higher surface energy density. Because of the periodic space, the number of horizontal dangling bonds is proportional to the tilting angle $\theta$. Tilting the plane by $-\theta$ and $\theta$ are degenerate. So, the increase of the surface energy is

$$\Delta E_s = \alpha |\theta|.$$  \hspace{1cm} (3.4)
This expression shows that the surface energy density has a cusp at $\theta = 0$.

It may be useful to note that $|\theta| = |\hat{A}_\parallel \cdot \hat{n}|$ for small theta, where $\hat{A}_\parallel$ is the direction of the horizontal dangling bonds. This can be generalized to a more general situation. With this, we know there are many cusps in the surface energy densities of the form discussed in the previous section.

### 3.3.3 Conventional Derivation of Surface Energy Density

The surface energy density $\gamma(\hat{n})$ has been defined to be the surface energy per unit area of a surface with a macroscopic average normal $\hat{n}$. In the case of nearest neighbor interaction, it can be written as

$$\gamma(\hat{n}) = \lim_{S_n \to \infty} \frac{N_n J}{S_n},$$

where $S_n$ is the area of the surface projected along the direction normal to $\hat{n}$, $N_n$ is the total number of bonds cut by the surface. All bond strengths have been assumed to be identical to $J$ for simplicity.

In crystals, the surface energy densities are conventionally derived in the following way.

First, take a plane normal to $\hat{n}$. This plane cuts atomic bonds connecting the atoms on different sides of the plane. Denote the atomic bonds by $A_\alpha$'s. The total number of bonds cut by the plane is then $\sum_\alpha |A_\alpha \cdot \hat{n}| S_n n_\alpha$, where $S_n$ is the area of this plane. $n_\alpha$ is the density of pairs of atoms connected bond $A_\alpha$. Therefore, the surface energy density is

$$\gamma(\hat{n}) = \lim_{S_n \to \infty} \frac{\sum_\alpha |A_\alpha \cdot \hat{n}|}{S_n} \frac{S_n J}{S_n}$$
In fact, the properties of crystals are not used during this derivation. Instead, the density \( n_\alpha \) has been implicitly assumed to be uniform. This assumption is not always valid even in crystals.

As we have shown, term \( |A_\alpha \cdot \hat{n}| \) indicates there is a cusp in the direction normal to \( A_\alpha \). These cusps lead to facets in the equilibrium shape. In other word, crystals with surface energy density of the form of Eq.(3.6) always have facets in their \( T = 0 \) equilibrium shapes.

### 3.3.4 A Sufficient Condition for Faceting in \( T = 0 \) Equilibrium Shapes

In this section, we shall give a more rigorous derivation of the surface energy density. During the course of this derivation, we shall find a sufficient condition for faceting in the \( T = 0 \) equilibrium shape.

Consider a macroscopically flat surface \( \Sigma \) with average normal \( \hat{n} \). Its total surface energy is given by

\[
E_s[\Sigma] = \int d^2 r_> d^2 r_< \rho(r_>) \rho(r_<) J(r_> - r_<) \\
= \int J(A) \Omega(A, \Sigma) d^3 \nu(r, A),
\]

(3.7)

where \( r_>, r_< \) are vectors on different sides of the surface \( \Sigma \), \( 2J(A) \) is the interaction between atoms separated by \( A \), and \( \Omega(A, \Sigma) \) is the volume swept through by \( \Sigma \) when it is translated by \(-A\). The pair correlation function
\( \nu(r, A) \) is defined as
\[
\nu(r, A) \equiv \rho(r) \rho(r + A).
\] (3.8)

A perfect bond-oriented system is defined as a system in which the pair correlation function within the range of interaction \( A^* \) is of the form
\[
\nu(r, A) = \sum_{a} \delta(A - A_a) h(r, A_a), \quad A < A^*,
\] (3.9)
where \( \{A_a\} \) is a finite set of vectors. The function \( h(r, A_a) \) has value 0 and 1, which determine the appearance of pair of atoms connected by \( A_a \). There are many different systems satisfy this condition, such as crystals, perfect quasicrystals and "bond oriented glasses". Besides the bond orientational order, crystals and perfect quasicrystals have long range translational orders. However, there is not translational order in bond oriented glasses.

For a perfect bond oriented system, using Eq.(3.9), we have,
\[
E_s[\Sigma] = \sum_{a} J(A_a) \int_{\Omega(A_a, \Sigma)} d^3r \ h(r, A_a)
\equiv \sum_{a} J(A_a) < h(r, A_a) >_{\Omega(A_a, \Sigma)} \int_{\Omega(A_a, \Sigma)} d^3r,
\] (3.10)
where \( < \cdots >_{\Omega(A_a, \Sigma)} \) is the average over the volume \( \Omega(A_a, \Sigma) \). The implicit assumption made in the conventional derivation of the surface energy density is identical to assume that \( < h(r, A_a) >_{\Omega(A_a, \Sigma)} \) is independent of the surface \( \Sigma \), i.e.
\[
< h(r, A_a) >_{\Omega(A_a, \Sigma)} = h(A_a).
\] (3.11)
This is a crucial assumption. This assumption guarantees that the \( T = 0 \) is equilibrium shape has facets. So, for a perfect bond oriented system, we
have surface energy

\[ E_s[\Sigma] = \sum_{\alpha} J(A_\alpha) h(A_\alpha) \int_{\hat{n}(A_\alpha, \Sigma)} d^2r \]
\[ = \sum_{\alpha} J(A_\alpha) h(A_\alpha) |A_\alpha \cdot \hat{n}| S_n, \]  

(3.12)

where \( S_n \) is the area of the surface \( \Sigma \) projected onto the direction normal to \( \hat{n} \). The surface energy density is then given by

\[ \gamma(\hat{n}) = \sum_{\alpha} J(A_\alpha) h(A_\alpha) |A_\alpha \cdot \hat{n}| \]
\[ \equiv \sum_{\alpha} g_\alpha |A_\alpha \cdot \hat{n}|. \]  

(3.13)

From the previous proof in the last section, it is clear that the surface energy of this form has cusps in the direction normal to \( A_\alpha \). These cusps lead to facets in the \( T = 0 \) equilibrium shape. The sufficient condition for faceting in the \( T = 0 \) equilibrium shape of a perfect bond oriented system is that the average density of pairs of atoms connected by atomic bonds on the surface is same as that in bulk.

As we have seen, the translational order is not explicitly used during the derivation of this sufficient condition. So, it implies the possibility of that a positionally disordered system has facets in its \( T = 0 \) equilibrium shape. Unfortunately, it is not completely clear whether this sufficient condition implies the translational order in a perfect bond oriented system.

The perfect bond oriented systems satisfying the sufficient condition are referred as simple bond oriented systems[2]. Not all perfect bond systems are simple bond oriented systems. Crystals with single atom unit cells are simple bond oriented systems. However, crystals with multi-atom unit cells are
not although their $T = 0$ equilibrium shapes are faceted. The perfect quasicrystals and the quasiglasses are not simple bond oriented systems either, but their $T = 0$ equilibrium shapes are faceted. The later will be used to show that a positionally disordered system can still have facets in its $T = 0$ equilibrium shape. These facts indicate that our sufficient condition is only one of the sufficient conditions and is not a necessary one.

The sufficient condition may be satisfied in the icosahedral glasses because the positional disorder may smear out the difference of the densities of paired atoms in different part of the sample. In the next section, equilibrium shapes of the perfect bond oriented systems with icosahedral symmetries and satisfying the sufficient condition will be discussed. Comparison of these predicted shapes to the observed growth shapes show good agreement.
3.4 \( T = 0 \) Equilibrium Shapes of the Simple Bond Oriented Systems with the Icosahedral Symmetry

3.4.1 Growth Shapes and Equilibrium Shapes

Equilibrium shapes of solids are almost impossible to obtain in laboratories and in nature, with a few exceptions. The \(^4\text{He}\) solid in superfluid \(^4\text{He}\) is the only known example in which the equilibrium shape can be achieved utilizing the very efficient mass transport. On the other hand, many solids form faceted growth shapes during their growth processes. In principle, these faceted growth shapes will relax to their equilibrium shapes at temperature \( T \) although the relaxation times can be much longer than the experimentally accessible time period.

The equilibrium shapes also depend on temperature. If the temperature \( T \) is above the roughening temperatures \( T_R \)'s of all the facets, the equilibrium shape is a smoothly rounded one. It is completely faceted if \( T \) is below all \( T_R \)'s. When the temperature is in between, the equilibrium shape is partially faceted and partially round. It is very difficult to relate the growth shape to the equilibrium shape at finite temperatures.

However, the \( T = 0 \) equilibrium shapes are more closely related to the growth shapes. It is generally believed that the large growth facets also appear in the \( T = 0 \) equilibrium shape although there is lack of a rigorous proof. (Only \( T = 0 \) equilibrium shapes will be discussed in the rest of this
section. From now on, we shall simply refer the $T = 0$ equilibrium shape as the equilibrium shape when there is no confusion). The following is an argument for this relation[3].

As we know, the growth velocity of a facet $\Sigma$ is proportional to $e^{-\beta F}$, where $\Delta F$ is the difference in free energies after and before growth a step on the facet $\Sigma$. Suppose that the step energy density of forming a step on the facet $\Sigma$ is $\eta[\Sigma]$, and that the chemical potential is $\mu$. The free energy change associated with the growth a step with circumference $L$ and height $h$, is given by

$$\Delta F = \eta[\Sigma]L + \mu Lh.$$  \quad (3.14)

In order to compare the growth velocities $v_l$ and $v_s$ for a large and a small facet, one needs to compare the free energy changes for forming the same step on them. Subscripts $l$ and $s$ stand for large and small respectively. The dominant dependence of $\Delta F$ on orientation comes from the orientational dependence of the step energy density $\eta[\Sigma]$. The chemical potential is orientational independent. In general, the step energy density of a large facet is greater than those of smaller ones. Using Eq.(3.14), we have

$$\frac{v_s}{v_l} \propto \frac{e^{-\beta \Delta F_s}}{e^{-\beta \Delta F_l}} = e^{\beta (n_s-n_l)L} > 1.$$  \quad (3.15)

i.e. the small facet grow faster than the large one.

To illustrate this argument, let us consider a 2D square crystal in which the atoms interact through an attractive nearest neighbor interaction $J_1$ and an attractive next nearest neighbor interaction $J_2$. Assume $J_2 \ll J_1$. Then,
the equilibrium shape is an octagon with unequal edges as shown in Figure 3.4.

The 2D square crystal is shown in Figure 3.5. Atoms are located at the intersections of solid lines. The nearest interactions between atoms are represented by the solid lines. The dashed lines represent the next nearest neighbor interactions. From this Figure, one can find that \( \eta[\Sigma_i] = J_1 \) and \( \eta[\Sigma_s] = J_2 \). Using Eq.(3.15), we obtained the ratio of the growth velocities of the large and small facet,

\[
\frac{v_s}{v_l} \propto e^{\beta(J_1 - J_2) L}
\]

Since \( J_1 > J_2 \), we have \( v_s > v_l \).

Growth shapes of this crystal at different times \( t_0 < t_1 < t_2 \) are also shown in Figure 3.5. As the time goes on, the small growth facet becomes smaller and smaller because it grows faster than the adjacent large growth facets. Eventually, it will be eliminated. Figure 3.5 also shows how this small growth facet evolves into a sharp edge. However, the large growth facets still exist in the growth shape. Compare the “final” growth shape with the equilibrium shape, we find that the large growth facets also appear in the equilibrium shape. So, qualitative information about \( T = 0 \) equilibrium shapes of solids can be obtained from their growth shapes.

3.4.2 Examples of the \( T = 0 \) Equilibrium and Growth Shapes of Simple Bond Oriented Systems with Icosahedral Symmetry

A. Vertex Model
Figure 3.4: The $T = 0$ equilibrium shape of a $2D$ square crystal with attractive nearest and next nearest neighbor interactions.
Figure 3.5: A schematic illustration of how a growth shape evolves. Thin solid lines represent nearest neighbor bonds. Dashed lines represent next nearest neighbor bonds. Thick solid lines are the growth front at different time.
In the vertex model of the simple bond oriented system, the atoms are connected by the atomic bonds with equal length and along the vertex vectors (i.e. 5-fold axes) \( \{ V_i, i = 0, \ldots, 5 \} \) of an icosahedron (see Figure 2.1). (Form now on, we shall use \( n \)-fold axes when we refer to the \( n \)-fold axes of an icosahedron). The surface energy density is given by

\[
\gamma(\hat{n}) = g \sum_{i=0}^{5} |V_i \cdot \hat{n}|.
\]  

Using the algorithm described in section 3.-.-, we find the equilibrium shape is a triacontahedron as shown in Figure 3.6. It has 30 identical rhombic facets with their normals along the 2-fold axes. Since all equilibrium facets are of the same size, it is highly possible that the growth shape is same as the equilibrium one.

Experiments show a substantial amount of disorder preserving the bond orientational order but destroying the long range translational order in the icosahedral phase of Al\(_6\)Li\(_3\)Cu. The disorder might smear out the difference in the average density pair correlation functions at different part of the sample such that the sufficient condition for facet is satisfied. This vertex model might be responsible to the experimentally observed triacontahedral growth shape in the slowly growth icosahedral phase of Al\(_6\)Li\(_3\)Cu.

B. Edge Model

In this model, the atoms are connected by atomic bonds with same length and along the edge vectors (i.e. 2-fold axes) \( \{ E_i, i = 1, \ldots, 15 \} \) (see Figure 2.1).
Figure 3.6: The $T = 0$ equilibrium shape of a of the simple bond oriented system with bonds along the fivefold axes of an icosahedron.
Its surface energy density is given by

$$\gamma(\hat{n}) = g \sum_{i=1}^{15} |E_i \cdot \hat{n}|. \quad (3.18)$$

The $T = 0$ equilibrium shape implied by Eq. (3.18) is a great rhombic dodecahedron as shown in Figure 3.7. The $T = 0$ equilibrium shape is composed of 12 large dodecagonal, 20 small hexagonal and 30 even smaller square facets. They are along the 5-fold, 3-fold and 2-fold axes respectively. If the small hexagonal and square facets are eliminated during a growth process, the growth shape will be a dodecahedron as shown in Figure 3.1b. The normals of the growth facets will be along the 5-fold axes. The vertex vectors are of the same length and along the 3-fold axes.

This dodecagonal growth shape has been observed in the icosahedral phase of GaMgZn. A similar argument as in the case of vertex model can be applied here to related the equilibrium shape to the observed growth shape of GaMgZn.

C. Face Model

In this mode, the atomic bonds are of equal length and along the face vectors (i.e. 3-fold axes) $\{F_i, i = 1, 10\}$. The surface energy density is

$$\gamma(\hat{n}) = g \sum_{i=1}^{10} |F_i \cdot \hat{n}|. \quad (3.19)$$

The $T = 0$ equilibrium shape is a convex polyhedron as shown in Figure 3.8 which has 90 rhombic faces with two different sizes. Since the sizes of the two types of equilibrium facets are close, it is not clear whether the smaller one still appear in the growth shape. We have had not a prediction for its
Figure 3.7: The $T = 0$ equilibrium shape of a of the simple bond oriented system with bonds along the twofold axes of an icosahedron.
Figure 3.8: The $T = 0$ equilibrium shape of a of the simple bond oriented system with bonds along the threefold axes of an icosahedron.
growth shape. No similar shapes have been observed in the growth shape of any icosahedral phase.
3.5 Determination of the Surface Energy Densities and the $T = 0$ Equilibrium Shapes of 2D and 3D Perfect Quasicrystals

Perfect quasicrystal models are popular models for quasicrystal phases. Similar to crystals, perfect quasicrystals have long range translational order. Faceted $T = 0$ equilibrium shapes of quasicrystals are expected. Although the long range translational order is not essential to facets, it results in plane-like surfaces in quasicrystals. Each of these plane-like surfaces is a layer of tiles with one set of edges parallel to a common direction. A plane-like surface in a 2D perfect quasicrystal is shown in Figure 3.9. (In the 2D perfect quasicrystals, surfaces are actually 1D objects). These plane-like surfaces are of the lowest surface energy density among all surfaces in each perfect quasicrystal. They are energetically easier to form. We shall see later in this section that these surfaces of the lowest surface energy densities lead to facets in the $T = 0$ equilibrium shapes of perfect quasicrystals.

3.5.1 Two Dimensional Perfect Quasicrystals

Now, consider a 2D perfect quasicrystal which is obtained by using the dual method described in chapter I. First, we construct a dual grid by $m$ sets of equally spaced parallel lines given by

$$r \cdot k^{(i)} = n_i + f_i, \quad i = 1, \ldots, m. \quad (3.20)$$
Figure 3.9: A set of plane plane-like surface in a 2D decagonal perfect quasicrystal model.
Each of these lines is referred as the dual grid line. \( \{ k^{(i)} \} \) is a set of normal vectors of these dual grid lines. The spacing of lines in each set is \( 1/|k^{(i)}| \).

Then, choose the real space spanning set \( \{ a^{(i)} \} \) such that

\[
\sum_{i=1}^{m} k^{(i)} a^{(i)} = \delta_{\mu\nu}.
\]

(3.21)

The atoms of the 2D quasicrystal are located at the vertices of the resulting 2D quasilattice. The atoms interact through the atomic bonds \( \{ a^{(i)} \} \). So, the surface energy of a macroscopically flat surface is the number of bonds cut by the surface multiplied by the bond strength.

Each bond in the real space corresponds to an edge shared by two polygonal regions in the dual space. For any given macroscopic flat surface \( \Sigma \) in the real space, there is a unique corresponding surface \( \Sigma_d \) in the dual space determined by the bonds cut by \( \Sigma \). The surface \( \Sigma_d \) is composed of line segments of the dual grid lines. The number of line segments of \( \Sigma_d \) is same as the number of bonds cut by \( \Sigma \). If the two ends of the surface \( \Sigma \) are pinned, the surface with lowest surface energy is given by the \( \Sigma_d \) in the dual space with corresponding pinned ends and minimal number of line segments. It is not difficult to find that the number of the line segments of \( \Sigma_d \) is same as the number of intersections between \( \Sigma_d \) and all dual grid lines. The surface \( \Sigma_d \) with minimal number of line segments is one puckering up and down around a straight line \( L_d \) with normal \( \hat{n}_d \). Now, the problem of counting number of bond cut by the surface \( \Sigma \) has been transformed to a simpler problem of counting the the number intersections of between the line \( L_d \) in dual space and all dual grid lines. The intersections between \( L_d \) and the dual grid lines
in one set are equally spaced with spacing \(1/|k^{(i)}| \sin \theta_i\), where \(\theta\) is the angle between normal of \(L_d\) and \(k^{(i)}\). Therefore, the number of intersections, \(\eta(\hat{n}_d)\), between \(L_d\) and all dual grid lines is given by

\[
\eta(\hat{n}) = \sum_{i=1}^{m} \eta_i(\hat{n}_d) = \sum_{i=1}^{m} |\hat{n}_d \times k^{(i)}|.
\]  

(3.22)

The length and the normal of the line \(L_d\) in the dual space are same as the those of the line connecting the two ends of the surface \(\Sigma\) in the real space. It can be proved as follows.

The normal vector of the line connecting the two ends of the surface \(\Sigma\) is same as the average normal of \(\Sigma\). This line can be expressed as

\[
S = \hat{S} \times \hat{t} z.
\]  

(3.23)

Similarly, the vector from one end of the line segments \(L_d\) to the other is

\[
S_d = S_d \hat{n}_d \times \hat{z},
\]  

(3.24)

where \(S_d\) is the length of the \(L_d\), \(\hat{z}\) is the unit vector perpendicular to the \(2D\) dual space. Then, the vector connecting the two ends of \(\Sigma\) is given by

\[
S = \sum_i \eta_i(\hat{n}_d) S_d a^{(i)} \text{sgn}(k^{(i)} \cdot \hat{n}_d \cdot \hat{z})
= S_d \sum_i \eta_i(\hat{n}_d) a^{(i)} \text{sgn}(k^{(i)} \times \hat{n}_d \cdot \hat{z})
= S_d \sum_i (\hat{n}_d \times k^{(i)}) a^{(i)} \frac{k^{(i)} \times \hat{n}_d \cdot \hat{z}}{|k^{(i)} \times \hat{n}_d \cdot \hat{z}|}
= S_d \sum_i a^{(i)} (k^{(i)} \times \hat{n}_d \cdot \hat{z})
= S_d \sum_i a^{(i)} k^{(i)} \cdot (\hat{n}_d \times \hat{z})
= S_d \hat{n}_d \times \hat{z}.
\]  

(3.25)
In the last step, the completeness relation Eq.(3.21) has been used. Since \( \hat{n}_d \) is perpendicular to \( \hat{u} \), we have \( |S| = S_d \) from Eq.(3.25). Compare Eq.(3.25) and Eq.(3.23), we have \( \hat{n} = \hat{n}_d \).

With these relations, the surface energy density \( \gamma(\hat{n}) \) can be calculated as follows.

\[
\gamma(\hat{n}) = \frac{\sum_{i=1}^{m} \eta_i(\hat{n}_d)J}{S}
= \sum_{i=1}^{m} m\eta(\hat{n})J
= J \sum_{i=1}^{m} |k^{(i)} \times \hat{n}|,
\]

(3.26)

where \( J \) is the bond strength, \( S \) is the length of the surface \( \Sigma \) projected to the line normal to \( \hat{n} \). There cusps along the directions of \( \{k^{(i)}\} \). Therefore, the normal of facets are also along the these direction which are the average normal directions of the plane-like surfaces.

As an example, the \( T = 0 \) equilibrium shape of a 2D decagonal perfect quasicrystal is presented in Figure 3.10. The normal vectors used in the dual method are \( k^{(i)} = k(\cos \frac{2\pi i}{5} \hat{x} + \sin \frac{2\pi i}{5} \hat{y}), \quad i = 0, \ldots, 4 \)

### 3.5.2 Three Dimensional Perfect Quasicrystals

A strong motivation for calculating the \( T = 0 \) equilibrium shape of 3D perfect quasicrystals is to compare them with the observed growth shapes of the icosahedral phases. The equilibrium shapes have been calculated by [7,2]. A general scheme of calculation the surface energy density of any 3D perfect crystal generated by the dual method gives in the paper by Ho, Jaszczak,
Figure 3.10: The $T = 0$ equilibrium shape of the decagonal perfect quasicrystal.
Li, and Saam[2]. It will be presented here in detail. Then, it will be applied to the calculation of the equilibrium shapes of different perfect quasicrystal models with the icosahedral symmetry.

A 3D perfect quasicrystal is constructed using the dual method as follows. The dual grid is composed of \( m \) sets of equally spaced parallel planes normal to \( \mathbf{k}^i \). These planes are given by

\[
\mathbf{r} \cdot \mathbf{k}^{(i)} = n_i + f_i \quad i = 1, \ldots, m.
\]  

These planes are referred as the dual grid planes. The dual grid planes divide the dual space into polyhedral regions. A set of phases \( \{f_i\} \) is chosen so that there are no more than three dual grid planes intersecting at the same point. The spacing of planes in each set is \( 1/|\mathbf{k}^{(i)}| \). We choose the real space spanning set \( \{a_i\} \) such that it satisfies the completeness relation:

\[
\sum_{i=0}^{m} k_{\mu}^{(i)} a_{\nu}^{(i)} = \delta_{\mu\nu}.
\]  

Atoms of the 3D perfect quasicrystal are located at the lattice points \( \sum_{i=1}^{m} n_i a^{(i)} \) of the resulting 3D quasilattice. The bonds \( \{a^{(i)}\} \) in the quasilattice represent the nearest neighboring intersections.

Each of these bonds in the real space corresponds to a polygon shared by two polyhedral regions in the dual space. For a macroscopically flat surface \( \Sigma \) with an average normal \( \mathbf{n} \) in the real space, this relation uniquely determines a surface \( \Sigma_d \) in the dual space according to the bonds cut. The surface \( \Sigma_d \) is composed of many polygonal patches, each of which is a portion of a dual grid plane. The number of bonds cut by \( \Sigma \) is equal to the number of polygonal
patches \((F)\) on \(\Sigma_d\). Because there are no more than three dual grid planes intersecting at a single point, every vertex on \(\Sigma_d\) connects to exact 4 edges of the polygonal patches. Therefore, the numbers of edges \((E)\) on \(\Sigma_d\) is twice of the numbers of vertices \((V)\) on \(\Sigma_d\), i.e. \(E = 2V\). Using the Euler theorem \((F + V - E = 1)\), we have \(F = V\). Because \(V\) and \(F\) are larger numbers, 1 is negligible. Therefore, the number of bonds cut by \(\Sigma\) is equal to the number of vertices on the surface \(\Sigma_d\) in the dual lattice.

The surface energy \(\gamma(\hat{n})\) is defined to be the surface energy density of the surface \(\Sigma\) with an average normal \(\hat{n}\) cutting least numbers of bonds. It corresponds to a \(\Sigma_d\) puckering up and down about a plane \(P(\hat{n}_d)\) with normal \(\hat{n}_d\). The intersections of the plane \(P(\hat{n}_d)\) with the dual grid planes divide \(P(\hat{n}_d)\) into polygonal regions. The vertices on the plane \(P(\hat{n}_d)\) have a one-to-one correspondence to the vertices on the surface \(\Sigma_d\). So, the number of bonds cut by \(\Sigma\) in the real space is equal to the number of vertices on the plane \(P(\hat{n}_d)\). The density of vertices formed by \(P(\hat{n}_d)\) and two sets of dual grid planes is

\[
\eta_{ij}(\hat{n}_d) = |\hat{n} \cdot k^{(i)} \times k^{(j)}|.
\]  

(3.29)

Then, the total number of bonds cut by \(\Sigma\) is \(\Gamma(\hat{n}) = S_d \sum_{i<j} \eta_{ij}(\hat{n}_d)\), where \(S_d\) is the area of the plane \(P(\hat{n}_d)\) in the dual space. The surface energy density \(\gamma(\hat{n}) \equiv \Gamma(\hat{n})/S\), where \(S\) is the area of the surface \(\Sigma\) projected to the plane normal to its average normal \(\hat{n}\).
The total oriented area of the surface $\Sigma$ is

$$
S = \sum_{i<j} S_d \eta_{ij} (\hat{n}_d) a^{(i)} \times a^{(j)} \text{sgn}(\hat{n}_d \cdot k^{(i)} \times k^{(j)})
$$

$$
= S_d \sum_{i<j} a^{(i)} \times a^{(j)} |\hat{n}_d \cdot (k^{(i)} \times k^{(j)})| \frac{\hat{n}_d \cdot (k^{(i)} \times k^{(j)})}{|\hat{n}_d \cdot (k^{(i)} \times k^{(j)})|}
$$

$$
= S_d \sum_{i<j} a^{(i)} \times a^{(j)} (k^{(i)} \times k^{(j)}) \cdot \hat{n}_d
$$

$$
= S_d \hat{n}_d.
$$

(3.30)

The completeness relation Eq.(3.28) has been used in the last step. This indicates that the average normal $\hat{n}$ of the surface $\Sigma$ is identical to the normal of the plane $P(\hat{n}_d)$ and that the projected area $S$ of the surface $\Sigma$ is equal to $S_d$.

The surface energy density of the 3D perfect quasicrystal is given by

$$
\gamma(\hat{n}) = \frac{S_d \sum_{i<j} \eta_{ij} (\hat{n}_d)}{S}
$$

$$
= \sum_{i<j} \eta_{ij}
$$

$$
= |\hat{n} \cdot k^{(i)} \times k^{(j)}|.
$$

(3.31)

This surface energy density has cusps in the directions of $k^{(i)} \times k^{(j)}$. These cusps lead to facets in the $T = 0$ equilibrium shape of the perfect quasicrystal.

In icosahedral perfect quasicrystals, $\{k^{(i)}\}$ has the icosahedral symmetry. They can be along 5-fold, 2-fold or 3-fold axes. Due to the icosahedral symmetry, $k^{(i)} \times k^{(j)}$ formed by different pairs of $k^{(i)}$ and $k^{(j)}$ may be along the same direction. Consequently the number of cusps and the number of facets are smaller than the number of ways to pair $k^{(i)}$ and $k^{(j)}$. The $T = 0$
equilibrium shapes of these icosahedral perfect quasicrystal are presented in
the following.

A. Vertex Model

In this model, the set of normal vector is chosen as

$$k^{(i)} = k \hat{v}_i, \quad i = 0, ..., 5,$$

where \(\{\hat{v}_i\}\) are along the 5-fold axes. Using the symmetry properties of \(\{\hat{v}_i\}\),
the surface energy density can be rewritten as

$$\gamma(\hat{n}) = J k^2 g \sum_{i=1}^{15} |\hat{n} \cdot \hat{e}_i|,$$

where \(\{\hat{e}_i\}\) are along the 2-fold axes, \(g = 2/\sqrt{5}\). This form of the surface
energy density allows directly using the algorithm developed in the previous
section. The equilibrium shape is a great rhombicdodecahedron as shown in
Figure 3.7 in the last section. As we discussed there, this equilibrium shape
may evolve into a dodecahedral growth shape which has been observed in
GaMgZn. This results in difficulty to use the growth shape to find whether
the simple bond oriented system or the perfect quasicrystal is a better model
for the quasicrystal phases.

B. Edge Model

In this model, the set of normal vectors is

$$k^{(i)} = k \hat{e}_i, \quad i = 1, ..., 15,$$

where \(\{\hat{e}_i\}\) are along the 2-fold axes. Similarly, we rewrite the surface energy
density as

\[ \gamma(\hat{n}) = g k^3 \sum_{\mu=1}^{3} g^{(\mu)} \sum_{i} |\hat{n} \cdot \hat{A}_i^{(\mu)}|, \]  

(3.35)

where \( \mu = 1, 2, 3 \) represents 5-fold, 2-fold and 3-fold axes, \( g^{(1)} = 5(\sin \pi/5 + \sin 2\pi/5) \), \( g^{(2)} = 1 \), \( g^{(3)} = 3 \sin \pi/3 \). The equilibrium shape is complicated polyhedron as shown in Figure 3.11. It contains 30 large 2-fold facets and other much smaller facets. During a growth process, those smaller facets may be eliminated. Then, the growth shape is a triacontahedron same as the prediction by the vertex model of the simple bond oriented system. This again makes it more difficult to interpret the observed growth shape of Al₆Li₃Cu.

C. Face Model

The set of normal vectors in this model is given by

\[ k^{(i)} = k \hat{f}^{(i)}, \quad i = 1, ..., 10, \]  

(3.36)

where \( \{\hat{f}^{(i)}\} \) are along the 3-fold axes. Again, we rewrite the surface energy density as the following form

\[ \gamma(\hat{n}) = J k^3 \sum_{\mu=1}^{3} g^{(\mu)} \sum_{i} |\hat{n} \cdot \hat{A}_i^{(\mu)}|, \]  

(3.37)

where \( \{\hat{A}_i^{(1)}\} \) are along the 2-fold axes with \( g^{(1)} = \frac{2}{3} \), and \( \{\hat{A}_i^{(2)}\} \) is a set of 60 icosahedral symmetry related vectors which are neither along the 5-fold nor the 3-fold axes, \( g^{(2)} = \frac{\sqrt{3}}{3} \). The equilibrium shape is a very complicated polyhedron as shown in Figure 3.12. If only largest equilibrium facets occur in its growth shape, it will be a icosahedron which has not been observed in any growth shape of icosahedral phase.
Figure 3.11: The equilibrium shape of the edge model of the icosahedral perfect quasicrystal.
Figure 3.12: The equilibrium shape of the face model of the icosahedral perfect quasicrystal
3.6 \( T = 0 \) Equilibrium Shapes of The Icosahedral Quasi-glasses

In section 3.4, we derived a sufficient condition for faceting in the \( T = 0 \) equilibrium shape of perfect bond oriented systems. This sufficient condition does not explicitly require long range translational order. However, we have not been able to prove that the sufficient condition does not imply long range translational order. Meanwhile, we have not found a model structure which satisfies this sufficient condition but does not have long range translational order. In order to prove the conjecture that translationally disorder systems can have faceted \( T = 0 \) equilibrium shape, we shall construct explicit examples referred as quasiglasses which are translationally disordered but have completely faceted \( T = 0 \) equilibrium shapes. These quasiglasses still have long range orientational order.

The quasiglass is constructed using the generalized dual method described as follows. Every step is the same as the dual method used to construct the perfect quasicrystal, except that the dual grid is composed of dual grid planes (or lines in 2D) for which the spacing randomly takes on values between \( d - \Delta \) and \( d + \Delta \). The average spacing between dual grid planes \( d = 1/|k^{(i)}| \) for the \( i^{th} \) set, where \( k^{(i)} \) is a vector normal to this set of planes. The fluctuation of the spacing over a long distance \( L \) is proportional to \( L^{\frac{1}{2}} \).

The atoms are located at the vertices of the resulting random lattice, which are still connected by the bonds \( \{a^{(i)}\} \). The completeness relation
Eq. (3.28) is still valid. Having gone through all the same steps of the calculation of the surface energy of the perfect quasicrystal, we find that the surface energy of a macroscopic flat surface with an average normal \( \hat{n} \) and projected area \( S \) is given by

\[
E_s(\hat{n}) = S \sum_{i<j} |\hat{n} \cdot k^{(i)} \times k^{(j)}| + O(S^{\frac{1}{2}}),
\]

(3.38)

where the term of the order of \( S^{\frac{1}{2}} \) is due to the fluctuation of the spacing of the dual grid planes. This term does not contribute to the surface energy density. The surface energy density is

\[
\gamma(\hat{n}) = \lim_{S \to \infty} \frac{E_s(\hat{n})}{S} = \sum_{i<j} |\hat{n} \cdot k^{(i)} \times k^{(j)}| + \lim_{S \to \infty} O(S^{-\frac{1}{2}})
\]

(3.39)

If the normal vectors \( \{k^{(i)}\} \) are chosen to be 5-fold, 2-fold or 3-fold axes, the \( T = 0 \) equilibrium shapes are identical to those given in the last section.

The bond orientational order is preserved in the quasiglasses because all the atomic bonds are same as those in the corresponding perfect quasicrystals. However, the long range translational order is destroyed. Therefore, the diffraction peaks no longer have \( \delta \)-function shapes. In the Figure 3.13, a pair of corresponding peaks of a 2D perfect quasicrystal and a 2D quasiglass is shown. These peaks are calculated numerically. Large size (~ \( 7.5 \times 10^5 \) tiles) quasilattice and quasiglass have been used in these calculations. From figure 3.13, it is clear the long range translational order is indeed destroyed in
the quasiglass. The \( \delta \)-function peak breaks into a set of much weaker peaks with finite widths.

However, the absence of the long range order does not destroy the plane-like surfaces. A set of such surfaces with common average normal in the same 2D quasiglass are shown in Figure 3.14. Although these surfaces have relatively large deviations from a straight line (or a plane in 3D), they still have a common average normal, and their fluctuations of the deviations over a large distance \( L \) is proportional to \( L^{1/2} \). The surfaces are the surfaces of the lowest surface energy density. Similar to what we discussed before, these energetically easier to form plane-like surface are the origin of the facets in the \( T = 0 \) equilibrium shapes of the quasiglasses. These examples explicitly show that translationally disordered systems can have faceted \( T = 0 \) equilibrium shape.
Figure 3.13: Comparison of a peak in the 2D decagonal perfect quasicrystal and the corresponding peak in the 2D decagonal quasiglass. a) A diffraction peak of a 2D decagonal perfect quasicrystal. b) The corresponding peak in the 2D quasiglass.
Figure 3.14: The plane-like surface in the same quasiglass
References


[3] This is pointed out to me by W. F. Saam.


LIST OF REFERENCES

Chapter I


14 P. M. Horn, W. Malzfeldt, D. P. Divincezo, J. Toner, and R. Gambino, 

15 S. Idziak, P. A. Heiny, and P. A. Bancel, Proceeding of International 
Workshop on Quasicrystals, Beijing, Sept. 1987

A117, 421(1986)

47, C3-351(1986)

18 See footnotes 65 and 67 on page 311-312 of ref.2

19 T. L. Ho, J. Jaszczak, Y. H. Li, and W. F. Saam, Phys. Rev. Lett. 59, 
1116(1987)


29 D. S. Rokhsar, N. D. Mermin, and D. C. Wright, Phys. Rev. B35, 
Rev. Lett. 58, 2099(1987)

30 D. S. Rokhsar, D. C. Wright, and N. D. Mermin, to be published

35 J. Jaszczak, B. Yang and W. F. Saam, preprint
39 See page 21 and the footnote on the page in Ref.2
41 T. H. Ho, private communication
42 See Chapter 7 of Ref.2 and references therein.

Chapter II

9 S. Idziak, P. A. Heiney, and P. A. Bancel, Proceeding of International Workshop on Quasicrystals, Beijing, Sept. 1987


Chapter III


3 This is pointed out to me by W. F. Saam.

4 G. Wulff, Z. Kristallogr. 34, 449(1901)

5 C. Herring, Phys. Rev. 82, 87(1951)
