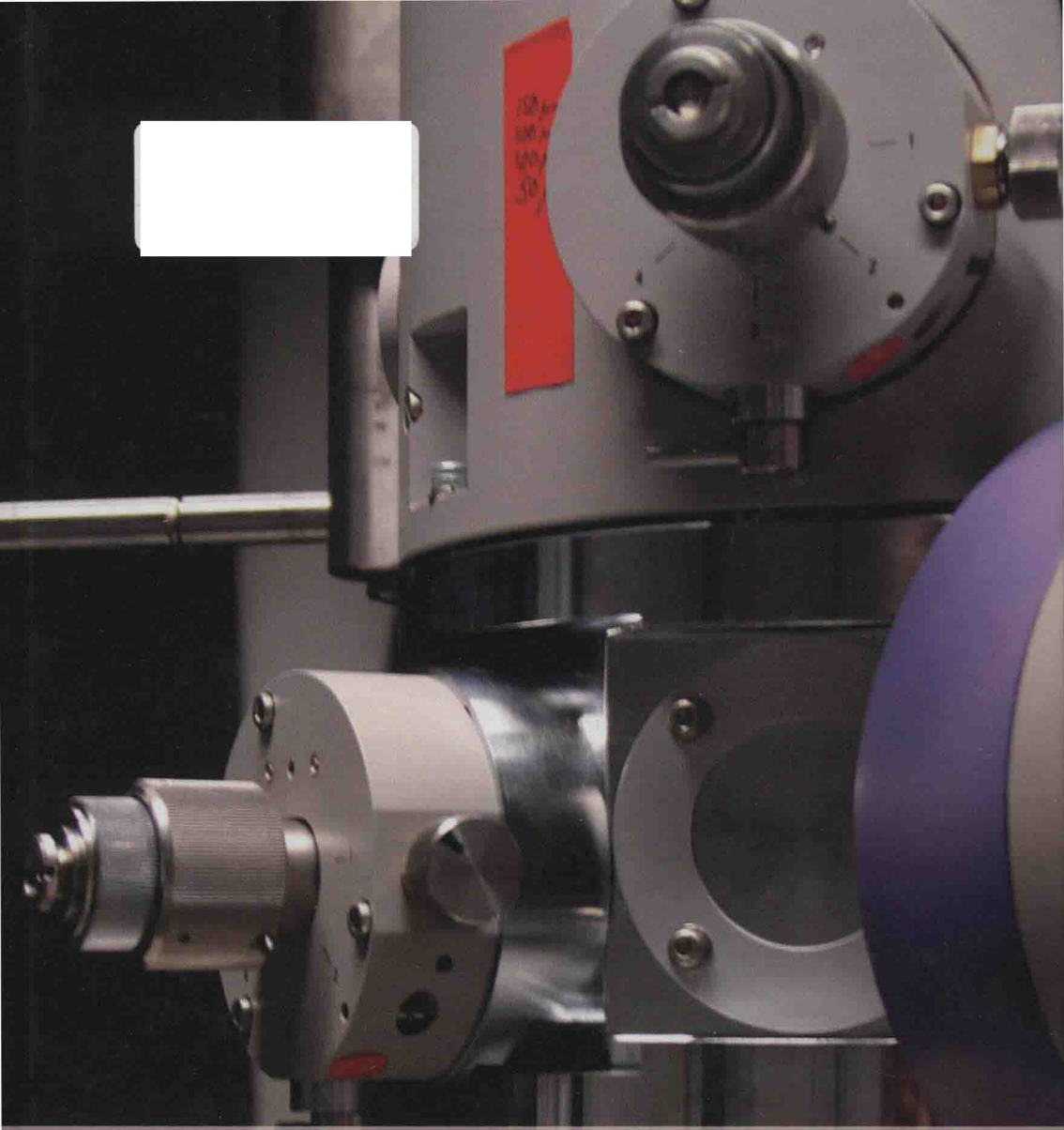

Handbook of Transmission Electron Microscopy

Lisa Page

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Edited by **Lisa Page**

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Preface

The purpose of the book is to provide a glimpse into the dynamics and to present opinions and studies of some of the scientists engaged in the development of new ideas in the field from very different standpoints. This book will prove useful to students and researchers owing to its high content quality.

This book compiles various research papers written by experts and scientists. It is a comprehensive summary of the various features of Transmission Electron Microscopy (TEM), from fundamental mechanisms and diagnosis to the recent developments in this area. This book discusses electron microscopy, new techniques for projection of images, experimental techniques for the study of nanomaterials, among others. The book also elucidates theoretical and practical aspects of modern microscopy techniques and the usage of TEM in material characterization. It will be beneficial for students, scientists, engineers and researchers working in this field.

At the end, I would like to appreciate all the efforts made by the authors in completing their chapters professionally. I express my deepest gratitude to all of them for contributing to this book by sharing their valuable works. A special thanks to my family and friends for their constant support in this journey.

Editor

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1

Indexing of Electron Diffraction Patterns of Icosahedral and Decagonal Phases

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1. Introduction

The atomic arrangements of solids fall into two broad categories. First refers to long range translational order giving rise to sharp diffraction patterns. Second relates to an atomic order that displays diffuse halos. Prior to the discovery of Quasiperiodic translational order in rapidly solidified Al-Mn alloys [1], sharp diffraction peaks were considered to be synonymous to possession of periodic translational orders in solids. The electron diffraction patterns reported in reference [1] were found to be invariant under icosahedral point group ($m\bar{3}\bar{5}$) symmetry. Any elementary text on crystallography begins by showing that 5-fold symmetry is incompatible with periodic lattice translations. Thus, it was proved beyond doubt that Shetchman et al.[1] have discovered a new state of order in solids. Readers may go through the notes given in annexure **A** for the excitement and importance of this discovery. The underlying atomic arrangement [1] was believed to possess "Quasiperiodic" translational order and due to invariance of diffraction patterns under icosahedral point group, such a class of solids was later termed as icosahedral quasicrystals (IQC). If one observes the location of diffracted spots in this class of solids then it is not periodic but all of them are as sharp as any crystalline diffraction patterns. These observations clearly established the fact that IQC displays new type of long range translational order known as Quasiperiodic translational order. We refer the readers to the annotations and reprints of papers in reference [2] for getting familiar with all the terminologies in this area. Having recorded diffraction patterns, the first step is to index them. For indexing, we need a set of basis vectors that are integrally independent. All three dimensionally periodic solids need three integrally independent basis vectors to index their diffraction patterns. The minimum number of integrally independent basis vectors is known as rank of any solids possessing long range translational orders [3-4]. Thus, all 3d periodic solids have rank equals to three. Remember, one uses four basis vectors for hexagonal crystals in Miller-Bravais (MB) scheme but all of them are not independent. As a consequence of this, assignment of indices to a diffracted spot in MB scheme is made unique by invoking condition that sum of indices along the three planar basis vectors is zero. We shall deliberate on this aspect further while discussing indexing of decagonal quasicrystals (DQC).

All Quasiperiodic structures possess rank greater than three. This is true even for incommensurate structures. However, quasicrystals diffraction patterns are invariant under

non-crystallographic point groups that are incompatible with periodic lattice translations. We do not propose to discuss this aspect further and interested readers may refer to international tables on crystallography [5] for subtle distinction between these phases. IQC are three dimensional (3d) quasicrystals whose diffraction patterns are invariant under icosahedral point group. For the purpose of indexing, one requires six integrally independent basis vectors parallel to the vertex vectors of an icosahedron. Thus, 3d IQCs have rank equals to three. We shall demonstrate that all the diffraction spots can be indexed with the help of sextuplets of indices. For spanning the entire reciprocal space one has to follow the rules of addition and subtraction. This is true for all reciprocal lattices. In addition to this, Quasiperiodic reciprocal lattices require inflation and deflation of vectors. We shall show this as we progress. The Quasiperiodic lattice constant is determined with the help of first strongest diffraction spots along the basis vectors. Owing to quasiperiodicity, Quasiperiodic lattice constant is scale dependent. The concepts of inflation/deflation and scale dependent lattice constant are reflection of the fact that we are dealing with a new state of order. In fact both these concepts are related to golden mean $\tau = \frac{\sqrt{5}+1}{2}$ which is one of the roots of the equation $x^2 - x - 1 = 0$. Please note that the golden mean has many interesting properties like $\tau^2 = \tau + 1, \left(\frac{1}{\tau}\right) = \tau - 1, \tau^3 = 2\tau + 1$ *and so on.* IQC phases are related to such a number. This is due to the presence of 5-fold rotational symmetry. There are three 6d Bravais lattices for IQC and they are expected to give rise to three distinct icosahedral phases. These are (i) Simple IQC (SI), (ii) Body centered IQC (BCI) and (iii) Face centered IQC (FCI). Both SI and FCI phases are reported in literature but we shall restrict our discussion on SI only. The need of 6d cubic lattice in the structural description of IQC has been found to be essential and convenient in higher dimensional crystallography. It is therefore essential that we get familiarize with the concept and methodology related to higher dimensional crystallography. We shall demonstrate all the necessary aspects pertaining to this as we proceed.

Following the discovery of IQC, a new class of quasicrystals was found. This class of quasicrystals has 2d quasiperiodicity and 1d periodicity. Four popularly known DQCs have 2,4,6 and 8 layer periodicities along 10-fold axis and are designated as T_2, T_4, T_6 and T_8 phases respectively. The diffraction pattern displayed the presence of a unique 10-fold symmetry axis. Hence, this class of 2d QC was christened as decagonal quasicrystals. The discovery of decagonal phases [6-7] posed novel problems to their structural description and indexing. The rank of such a solid is five. Four basis vectors oriented with respect to each other by 72^0 and the fifth one perpendicular to this plane are sufficient to map the entire reciprocal space. However, a set of vectors related by five -fold symmetry may not possess quintuplet of indices that are permuted. These aspects are dealt extensively in references [8-9]. To attain permuted indices to refer to a set of vectors related by 5-/10-fold symmetries one uses six basis vectors [10]. The additional vector required to preserve symmetry in the indices for a family of directions/planes during indexing gives rise to the problem of redundancy. This refers to the non-unique assignment of indices to a diffraction spot. This can be surmounted by putting condition on indices akin to those of MB scheme for hexagonal crystal. We have recently discussed many novel aspects pertaining to this [9] by revisiting the MB indexing schemes of hexagonal [10-11], decagonal [8] and their related phases with the help of higher dimensional approach. For indexing diffraction patterns, one has to follow the approach of Copernican crystallography developed in Fourier space [3, 4].

In contrast, the canonical cut and project scheme [12-17] is capable of providing information about the atomic positions as well as the intensity of Quasiperiodic structures. We will not be deliberating on these in this chapter excepting succinctly dealing with the concepts of higher dimensional crystallography in the next section. Higher dimensional crystallography utilizes a mathematical construct for structural modeling of Quasiperiodic phases in a convenient way.

2. Elements of quasicrystallography

We need to remember that diffraction patterns offer the best way to define a lattice. We may understand this in the following way. If we ignore the intensity variation and replace all the diffracted spots by a point (for example, selected area electron diffraction pattern from a single grain) then we get arrangement of points in 2d section of a 3d reciprocal lattice. The prefix reciprocal before lattice appears because the distances are measured in terms of $Å^{-1}$. For describing atomic arrangements of solids one has to express distances in terms of Å and the underlying lattice is known as direct lattice. A lattice has a set of basis vectors whose integral linear combination helps us reach any diffracted spot with respect to the transmitted beam. Similar concept will hold for direct primitive lattice. The minimum number of integrally independent basis vectors required to accomplish this task is known as the rank of solids. Please note that the way we have introduced lattice does not demand anything other than the existence of diffraction patterns. Latter is a hard verifiable experimental fact. Selected area diffraction is the most convenient way to record single crystal like diffraction patterns from a polycrystalline specimen. Developing crystallography with the help of reciprocal space was central philosophy advocated earlier [18]. This concept was emphasized and extended further by N.D.Mermin (1992) after the discoveries of IQC, DQC and many other related phases [3-4]. If we observe three dimensional periodicities in diffraction patterns then we are dealing with the crystals of rank 3. The observation of incommensurate structures in 1977 [12] and their interpretation demanded four basis vectors instead of three. Incommensurate structures display crystallographic point group symmetry but their diffraction patterns possess aperiodicity in one of the three directions. In contrast, quasicrystals discovered by Shetchman et al. in 1984 displayed icosahedral point group symmetry [1] and aperiodicity of a special type. We call this as quasiperiodicity. In general, the existence of aperiodic order in a direction, demands at least two length scales that are relatively incommensurate. This is said in other words means the ratio of two fundamental lengths cannot be expressed as a rational number. We may understand this in a mathematical way as given below.

Let us consider a point on the line whose distance from an arbitrary origin is X_n. We define this by

$$X_n = a\left(n + (1/\tau)\lfloor (n/\tau) \rfloor\right) \tag{1}$$

Where the floor function $\lfloor x \rfloor$ of any number x is defined by the number x minus the fractional part of x. This means that floor function is basically the lowest possible integer of that number. As a consequence of this we realize that the two terms in the above equation are periodic independently with a period of a and (a/τ) respectively. H.Bohr has shown that equation (1) generates points that are almost periodic or Quasiperiodic [19-20]. The

floor function also ensures that the two consecutive points are not coming arbitrary close to each other. This is important for a real solid. There has to be a minimum distance of separation between two atoms.

Thus, we may write a general expression having aperiodicity as

$$X_{m,n} = a\left[m + n\tau\right] \tag{2}$$

Where, m and n are integers.

A simple calculation of X_n based on equation (1) generates points on a line that is well known Fibonacci series for τ = 1.618.....(golden mean). This is a quadratic irrational. As mentioned earlier, this is one of the two roots of equation $x^2 - x - 1 = 0$. Golden mean τ has a continued fraction representation: τ = 1+1/1+.....=1/1;2/1;3/2;5/3;8/5;13/8;21/13 and so on. These are the successive approximants of τ. One way to generate periodic structures of varying periods is by replacing τ by one of the above rational values. Such structures are known as rational approximants. We proceed to give alternative discussion of equations (1) and (2) in terms of higher dimensional crystallography.

Let us consider a set of points on one dimension of the type that we have been discussing so far. If we have to index each of the points on the lattice generated by equation (1) then we will do it conveniently by specifying two integers (m,n). Thus the rank of such a lattice is 2. Please note that the points are lying on a line. If this happens for a three dimensional solids in all the three directions then we will require 6 indices to indicate a point for such cases. Thus, the rank of such a solid will be 6. This is the case for IQC phase. Let us translate this discussion in terms of basis vectors. We shall first do it for the one dimensional Quasiperiodic case.

Let us consider two vectors V_1 and V_2 along a direction with unit vector x^{par} such that $V_1 = \cos\theta\, x^{par}$ and $V_2 = \sin\theta\, x^{par}$. Any vector on the line terminating at a lattice point is given by:

$$R = a(m_1\ V_1 + m_2\ V_2) \quad \text{and} \quad G = (1/a)(n_1\ V_1 + n_2\ V_2) \tag{3}$$

Where R and G are direct and reciprocal space lattice vectors; m_1; m_2 and n_1; n_2 are set of integers and a is spacing in Å. For direct space there has to be a minimum separation between two points as every lattice point is a probable location of atom. For reciprocal space this is not at all essential. If we choose $(\cos\theta / \sin\theta) = \tau$, then we have

$$R = a\sin\theta(m_1\tau + m_2) \quad \text{and} \quad G = (1/a)Sin\theta(n_1\tau + n_2) \tag{4}$$

The form of set of equations now resembles with those of equations (1) and (2). If we choose integers that are a combination of positive and negative both then there is an important difference between periodic solids and aperiodic ones. The set of points generated on the line is uniformly and densely filled. For R, this is obviously inconsistent. We commented earlier about the minimum distance of separation between two points. We also know from the experimental observations of IQC that in reciprocal space, we do observe sharp Bragg

peaks at discrete locations just like periodic crystals. Let us attempt to understand this through the language of higher dimensional crystallography. We construct a projection matrix (P) through the dot products of the basis vectors.

$$P = \{P_{ij}\} = \{V_{ij}\} = \{V_i . V_j\} \text{ where } P_{11} = \cos^2\theta;\ P_{22} = \sin^2\theta;\ P_{12} = \cos\theta\sin\theta$$

$$P = \begin{bmatrix} \cos^2\theta & \cos\theta\sin\theta \\ \cos\theta\sin\theta & \sin^2\theta \end{bmatrix} \tag{5}$$

Equation (5) satisfies $P^2 = P$. This is an important property of a projection matrix. Please note that the determinant of this matrix is zero and the trace is equal to 1. We can also define a matrix Q by the following relation:

$$Q = I - P = \begin{bmatrix} \sin^2\theta & -\sin\theta\cos\theta \\ -\sin\theta\cos\theta & \cos^2\theta \end{bmatrix} \tag{6}$$

Where I is an identity matrix of order 2. Please see that $Q^2 = Q$ and $PQ = 0$. All other properties of P are displayed by Q also. The space generated by this matrix is orthogonal to that of P.

If we choose another set of basis vectors W_1 and W_2 then we are in a position to define these on a line such that they are anti-parallel or at 180° with each other. Please note that in parallel space V_1 and V_2 are parallel. From the learning of matrix representation theory, we call the two spaces to be orthogonal. In terms of a unit vector x^{perp} we may write $W_1 = \sin\theta\ x^{perp}$ and $W_2 = -\cos\theta\ x^{perp}$.

We may define a orthonormal basis such that $V_i + W_i = e_i$ where i =1 to 2 and $e_i e_j = \delta_{ij}$ with $\delta_{ij} = 1$ for i=j and $\delta_{ij} = 0$ for $i \neq j$. The two basis vectors e_1 and e_2 are orthonormal and clearly represent the bases for a two dimensional space. With the help of two matrices given in equations (5 and 6), we can also write $V_i = P_{ij}\, e_j$ and $W_i = Q_{ij}\, e_j$ for i, j to vary from 1 to 2 only. The two dimensional direct lattice vector R^2 and reciprocal lattice vectors G^2 can now be written as:

$$R^2 = a\,(m_1e_1 + m_2e_2) \text{ and } G^2 = (1/a)(n_1e_1 + n_2e_2) \tag{7}$$

Where a can be identified as two dimensional lattice parameter of a square lattice. Let us designate now R and G as the components of Equation (7) in "V" space or "physical space" or "par space" and S and H as the components of Equation (7) in "W" space or "pseudo space" or "complementary space" or "perp space". All these terminologies are used in Quasicrystalline literature and we need not get frightened by them. They are given by

$$R = a\,(m_1V_1 + m_2V_2) \quad \text{and} \quad G = (1/a)(n_1V_1 + n_2V_2) \tag{8}$$

$$S = a\,(m_1W_1 + m_2W_2) \quad \text{and} \quad H = (1/a)(n_1W_1 + n_2W_2) \tag{9}$$

We get after substituting for V_i and W_i the following expressions:

$$R = a\sin\theta\,(m_1\tau + m_2)\ x^{par} \tag{10a}$$

$$G = (1/a)sin\theta\ (n_1\tau+n_2)\ X^{par} \tag{10b}$$

$$S = asin\theta\ (m_1 - m_2\tau)\ x^{perp} \tag{11a}$$

$$H = (1/a)sin\theta\ (n_1 - n_2\tau)\ x^{perp} \tag{11b}$$

We observe that the terms within the parentheses of equations (10a) and (10b) are of the same form as we have written earlier in equations (1) and (2). Are we getting any extra information by following the path that we have adopted in the latter part of the discussion? Yes, we can ensure minimum separation between two points in the direct lattice if we put a condition on the set of indices m_1 and m_2 with the help of equation (11a). Please recall that the floor function in equation (1) was helping us accomplish this task. The matrix formulation presented here can be generalized without any difficulty for two and three dimensional aperiodic structures or Quasiperiodic structures for our discussion.

As mentioned above, we demonstrate the method of ensuring minimum distance of separation between two points in parallel or physical direct space. We have a square 2d lattice (we call them as hyperlattice) having basis vectors e_1 and e_2 with lattice parameter *a*. We attach a line element to each of the lattice points. The length of the line element is $L^{perp}(say)$. Please note that (L^{perp}/a^2) is the linear density of points. We choose this based on the density of the points required for the purpose. This can be arrived at by referring to the density of the points needed for the related approximant structures. As stated earlier, structures that are generated by substituting τ by its successive approximants are termed as rational approximant structures. The α-Al-Mn(Fe)-Si cubic structure with space group Pm3 having lattice parameter of ~12.68Å and 138 atoms in the unit cell is one such example. This is described as (1/1) approximant of icosahedral structures in Al-Mn system. Please see annotations in reference [2] and also consult [21] for further details.

In cut and project scheme, the length of such a line element is taken as $L^{perp} = a\ (\sin\theta + \cos\theta)$. This is the external boundary of the shape in W-space obtained by projecting all the vertices of the higher dimensional unit cell on to it. We place it on the lattice point such that it is parallel to *perp.space* and is symmetric around it. This means the line element is extending both sides from $+(L^{perp}/2)$ *to* $-(L^{perp}/2)$. We may also work with the asymmetric setting by placing the line element having its extent from 0 to L^{perp}. The physical space line will cut this line element selectively and minimum separation between the two consecutive points can be ensured [14-16]. Now we would like to understand the *Fourier Transform (F.T.)* of the structure that we have generated. It is a combined effect of two distinct entities: the 2d square hyperlattice and the line element L^{perp} that is serving as motif in crystallographic parlance. Hence the *F.T.* of the 1d quasicrystals in physical space will be given by the convolution of the two functions. The *F.T.* of the 2d lattice will be a delta function and the weight of the delta function will be modulated by the *F.T.* of the line element. We therefore write:

F.T.of the 1d Quasicrystals = F.T. of the 2d lattice × F.T. of the line element

$$F.T.(G) = 1\times(1/L^{perp})\int_{-(L^{perp}/2)}^{(L^{perp}/2)} Exp(-2\pi iH.S)dS \tag{12}$$