INTRODUCTION TO FOURIER-SPACE CRYSTALLOGRAPHY

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1. Introduction

Inspired by the growing numbers and varieties of quasiperiodic crystals, the International Union of Crystallography has redefined the term *crystal* to mean "any solid having an essentially discrete diffraction diagram", thereby shifting the essential attribute of crystallinity from position space to Fourier space.[1] Within the family of crystals one distinguishes between periodic crystals, which are periodic on the atomic scale, and aperiodic crystals which are not. This broader definition reflects our current understanding that microscopic periodicity is a sufficient but not a necessary condition for crystallinity.

The purpose of this lecture is to describe the corresponding shift to Fourier space in the crystallographic classification scheme, proposed over thirty years ago by Bienenstock and Ewald[2] and established as a practical scheme for periodic and quasiperiodic crystals by Rokhsar, Wright, and Mermin.[3] I will emphasize that Fourier-space crystallography, which avoids an unnecessary detour into high-dimensional 'superspaces', is strongly based on 3-dimensional geometry, clarifies the concept of point group for aperiodic crystals, and provides a unified treatment for all types of crystals: periodic crystals, incommensurately modulated crystals, composite crystals, quasicrystals, and modulated quasicrystals.

2. The Bravais Class – A class of (reciprocal) lattices

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

$$\rho(\mathbf{r}) = \sum_{\mathbf{k} \in L} \rho(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}} \ . \tag{1}$$

The (reciprocal) *lattice L* – sometimes called the Fourier module – is defined as the set of all integral linear combinations of the wave vectors determined by the observed Bragg peaks. As so defined, L includes wave vectors at which the coefficients $\rho(\mathbf{k})$ are too weak to be detected. As the resolution is improved more peaks may appear at larger wave vectors and in the quasiperiodic case between

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[1] *Acta Cryst.* **A48** (1992), 928.

[2] *Acta Cryst.* **15**, (1962) 1253-1261.

[3] With later contributions also by Rabson, Dräger, and myself. A detailed list of references is given in the review by Mermin, *Rev. Mod. Phys.* **64**, (1992) 3-49, and more recent references are given at the end of these notes.

already existing peaks. This is because quasiperiodic lattices are 'dense' in the mathematical sense – there is no requirement of minimal distance between wave vectors. The lattice L may also include wave vectors at which $\rho(\mathbf{k})$ is required to vanish by the symmetry of the crystal. Such points are called extinctions and will be discussed later. It has been shown by Mermin[4] that there is no other generic reason for wave vectors in L to be missing from the diffraction pattern.

We normally restrict ourselves to lattices which can be generated by an integral linear combination of a *finite* number of wave vectors. The minimum number D of vectors needed to generate L is called the *rank* or indexing dimension of L. A crystal is *periodic* if and only if the rank of its lattice is equal to the physical dimension d. Only then is the lattice a conventional 'reciprocal lattice' related in the familiar way to a lattice of real-space translations under which the periodic crystal is invariant. We shall always use the term 'lattice' referring to the lattice of wave vectors and not to the 'direct lattice' of real-space translations.

The point group of the lattice – its holohedry – is the set of proper and improper rotations applied about the origin of Fourier space which leave it invariant. It is a finite subgroup of $O(3)$ which necessarily contains the inversion. Two lattices are in the same *Bravais class* if one can interpolate between them with a sequence of lattices, all with the same point group and rank.

Quasiperiodic crystals fall under three categories based on their Bragg peak intensities. The term *quasicrystal* is used for quasiperiodic crystals in which no clear distinctions can be made between the Bragg peaks based on their intensity (other than the trivial decay in intensity of high-indexed peaks). The diffraction patterns of *incommensurately modulated crystals* contain a single sublattice of strong reflections caused by an average (periodic or quasiperiodic) structure and a set of weak reflections caused by the modulations. Finally, *composite crystals* are composed of two (or more) interpenetrating subsystems producing two (or more) sublattices of strong reflections and a set of satellites which are due to the mutual interaction of the subsystems.

3. Indistinguishability and the concept of Point Group Symmetry

The point group of a periodic crystal is traditionally defined as the subgroup of the lattice point group which leaves the density itself invariant to within a translation. The densities of aperiodic crystals, however, in general possess no such symmetries. A careful examination shows that any region in a rotated aperiodic crystal can be found in the unrotated crystal, but the larger the region the further away you have to look in order to find it. The two crystals contain the same statistical distribution of substructures on all scales.

Exercise 1. *Show that if a two-dimensional crystal does contain more than a single point, about which an n-fold rotation brings it into perfect coincidence with itself, then the crystal is necessarily periodic.*

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[4] *Proceedings of the XIX International Colloquium on Group Theoretical Methods in Physics, Salamanca, Spain, 1992.* Vol. II, pp. 302-317.

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

$$\frac{1}{V} \int d\mathbf{r} \rho(\mathbf{r}_1 - \mathbf{r}) \ldots \rho(\mathbf{r}_n - \mathbf{r}) = \frac{1}{V} \int d\mathbf{r} \rho'(\mathbf{r}_1 - \mathbf{r}) \ldots \rho'(\mathbf{r}_n - \mathbf{r}) . \qquad (2)$$

This condition acquires a very simple form in Fourier space – the Fourier coefficients of two indistinguishable densities ρ and ρ' must be related by

$$\rho'(\mathbf{k}) = e^{2\pi i \chi(\mathbf{k})} \rho(\mathbf{k}) , \qquad (3)$$

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

Exercise 2. *Show that the Fourier transform (1) of condition (2) leads to an equivalent condition that the product of the density Fourier coefficients $\rho(\mathbf{k})$ over any set of wave vectors summing to zero should agree with the corresponding product for $\rho'(\mathbf{k})$. Show that the identity of the two- and three-point correlation functions is enough to guarantee the identity of all higher-order correlation functions by proving that the two indistinguishable densities are related by a gauge function as in (3).*

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

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

$$\rho(g\mathbf{k}) = e^{2\pi i \Phi_g(\mathbf{k})} \rho(\mathbf{k}) . \qquad (4)$$

Exercise 3. *To illustrate the use of phase functions, consider a 2-dimensional density constructed as a sum of five plane waves separated by angles of $\frac{2\pi}{5}$: $\rho(\mathbf{r}) = \sum_{n=1}^{5} \sin(\mathbf{k}_n \cdot \mathbf{r} + \phi)$, where $\mathbf{k}_n = \left(\cos(n\frac{2\pi}{5}), \sin(n\frac{2\pi}{5}) \right)$. Show that the density is 10-fold symmetric whenever ϕ is an odd-integer multiple of $\pi/10$. (Hint: Express the density in the form of Eq. (1), use the relation $-1 = e^{i\pi}$, and require that the phase function be linear.)*

Finally, since $\rho([gh]\mathbf{k}) = \rho(g[h\mathbf{k}])$, it follows from (4) that the set of phase functions associated with the elements of a point group G must satisfy the *group compatibility condition:*

$$\forall g, h \in G : \qquad \Phi_{gh}(\mathbf{k}) \equiv \Phi_g(h\mathbf{k}) + \Phi_h(\mathbf{k}). \tag{5}$$

These constraints on the phase functions are the generalizations to quasiperiodic crystals of the Frobenius congruences in the traditional space group description of periodic crystals.

Exercise 4. *Prove Eq. (5) and show, for example, that if g and h commute their phase functions must satisfy $\Phi_g([h-1]\mathbf{k}) \equiv \Phi_h([g-1]\mathbf{k})$.*

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4. The Space Group – A class of phase functions

Having defined the point group and the phase functions, the space-group classification of crystals is merely an organization of sets of phase functions into equivalence classes according to two criteria:

1. Gauge Equivalence. Two sets of phase functions, Φ and Φ', that describe indistinguishable densities ρ and ρ', related by a gauge function χ, should clearly be associated with the same space group. It follows from (3) and (4) that two such sets must be related by

$$\Phi'_g(\mathbf{k}) \equiv \Phi_g(\mathbf{k}) + \chi([g-1]\mathbf{k}) \tag{6}$$

for every g in the point group and every $\mathbf{k}$ in the lattice. We call phase functions describing indistinguishable densities *gauge-equivalent* and equation (6), converting Φ into Φ', a *gauge transformation.*

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

$$\Phi'_g(\mathbf{k}) = \Phi_{sgs^{-1}}(s\mathbf{k}) . \tag{7}$$

Exercise 5. *Operations s that are in the point group G have precisely this property, but show directly from (5) that for such s, Φ' and Φ are already gauge-equivalent.*

If s is *not* an element of the point group, then the two sets of phase functions will not in general be gauge-equivalent. In the periodic case s can be an element of $O(3)$ (for example a 90 degree rotation when G is a tetrahedral point group on a cubic lattice), or an element of $O(3)$ combined with a rescaling of the primitive lattice-generating vectors (for example 90 degree rotations of an orthorhombic lattice). Here the distinct gauge-equivalence classes making up a single space group are the different settings of that space group. In the quasiperiodic case s can be an isotropic rescaling of the entire lattice (as in icosahedral quasicrystals), an isotropic rescaling of a sublattice (as in axial quasicrystals), or even independent rescalings

of individual lattice-generating vectors. Because rescalings are often (though not always) a part of the transformation s, two classes of gauge-equivalent phase functions that are further identified in this manner are called *scale-equivalent*.

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

5. Gauge Invariant Phases – Screw axes, Glide planes, and Extinctions

It follows from Eq. (6) that if $g\mathbf{k} = \mathbf{k}$ then $\Phi_g(\mathbf{k})$ is invariant under arbitrary gauge transformations. These gauge-invariant phases are directly related to the phenomenon of *extinctions*, for it follows directly from the definition (4) of the phase function that whenever $g\mathbf{k} = \mathbf{k}$, the Fourier coefficient $\rho(\mathbf{k})$ vanishes unless $\Phi_g(\mathbf{k})$ also vanishes (modulo an integer). Thus the phase functions of a given space group immediately determine the extinctions.

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

Exercise 6. *(A) Use the group compatibility condition (5) to show that a phase function associated with a mirror m can only assume the values 0 and 1/2 in the invariant plane of the mirror. (Use the relation $m^2 = e$, where the identity e has by definition $\Phi_e \equiv 0$).*
(B) Show that a phase function associated with an n-fold rotation r can only assume the values j/n on the axis of rotation.

We call the plane of a mirror m a *glide plane* if $\Phi_m(\mathbf{k}) \not\equiv 0$ for any lattice vector in the plane. We call the axis of a rotation r a *screw axis* if $\Phi_r(\mathbf{k}) \not\equiv 0$ for any lattice vector on the axis. These definitions eliminate the need to associate extinctions with the interplay between rotations and translations which is peculiar to the periodic case. Moreover, the results obtained in Exercises 6 and 7, though geometrically trivial in the periodic case, are valid for aperiodic crystals of arbitrary (not necessarily finite) rank.

Exercise 7. *If an axis of n-fold rotation r lies in the plane of a mirror m then the product rm is also a mirror. Show that $\Phi_r(\mathbf{k})$ can only assume the values 0 and 1/2 on the axis of rotation. This establishes that screw axes of odd order cannot exist in mirror planes.*

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6. Enumeration – Basic Ideas and Selected Examples

1. Bravais Classes.

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

Consider next the cubic, tetrahedral, and icosahedral lattices of rank 6. It has been shown that all rank-6 cubic lattices are decomposable into two mutually incommensurate rank-3 (periodic) cubic lattices, *i.e.* they contain all integral linear combinations of vectors from the two lattices and nothing else. As such they are classified into six Bravais classes denoted as the sum of two rank-3 Bravais classes: $P + P$, $I^* + I^*$, $F^* + F^*$, $P + F^*$, $P + I^*$, and $I^* + F^*$ (the star is a reminder that these are all in Fourier space). There are three Bravais classes of rank-6 tetrahedral lattices which cannot be decomposed in such a way since we know that there are no tetrahedral lattices of rank 3. Lattices in these three Bravais classes are most simply described as integral linear combinations of the six vectors $(1, \pm\alpha, 0)$, $(0, 1, \pm\alpha)$, and $(\pm\alpha, 0, 1)$ with primitive, face-centered (the sum of all integers even) and body-centered (all integers of the same parity) indexing. When the irrational number α is equal to the golden mean these become the three Bravais classes of rank-6 icosahedral crystals.

Finally, consider the hexagonal and trigonal lattices of arbitrary (but finite) rank. It has been shown that all such lattices are fully decomposable into only three types of periodic building blocks: rank-1 sublattices along the axis of 3- or 6-fold symmetry, rank-2 triangular sublattices in the plane perpendicular to the axis of rotation, and – only in the trigonal case – rank-3 rhombohedral sublattices. To enumerate all hexagonal and trigonal Bravais classes of rank-n we simply consider all possible decompositions of n and all possible mutual orientations of the various sublattices.

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

2. Gauge Equivalence Classes.

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

Exercise 8. *Show that for centrosymmetric point groups there exists a gauge in which the phase function $\Phi_i(\mathbf{k})$, associated with the inversion, is zero everywhere. Show that in this gauge all the density Fourier coefficients $\rho(\mathbf{k})$ are real and therefore all other phase functions are restricted to the values 0 or 1/2.*

When the lattice is decomposable into a sum of sublattices of lower-rank, each independently invariant under the lattice point group, it is not even necessary to recompute the possible gauge-equivalence classes. All one needs to do is to consider all the different combinations of the gauge-equivalence classes already classified for the lower-rank sublattices. This is possible because the group compatibility condition (5) acts independently in each invariant sublattice and the choice of gauge is independent in each invariant sublattice. Using this principle, one for example, immediately deduces the gauge-equivalence classes for rank-6 cubic crystals or hexagonal and trigonal lattices of arbitrary finite rank from the well-known gauge-equivalence classes in the periodic case.

3. Scale Equivalence Classes.

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

When dealing with incommensurately modulated crystals or composite crystals one may wish to constrain the rescaling operations s to those which leave invariant the sublattice(s) of strong reflections. The finer categories that arise by imposing such a constraint are merely settings of the more general categories – the space groups. Different settings of a space group which are appropriate for the description of incommensurately modulated crystals or composite crystals are simply specified by identifying the sublattice(s) of strong reflections.

7. Acknowledgements

8. References

Listed here are only the references which are not listed in the review by N. D. Mermin, "The space groups of icosahedral quasicrystals and cubic, orthorhombic, monoclinic and triclinic crystals". *Rev. Mod. Phys.* **64**, (1992) 3-49.

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