

Quasicrystals: A Matter of Definition

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It is argued that the prevailing definition of quasicrystals, requiring them to contain an axis of symmetry that is forbidden in periodic crystals, is inadequate. This definition is too restrictive in that it excludes an important and interesting collection of structures that exhibit all the well-known properties of quasicrystals without possessing any forbidden symmetries.

KEY WORDS: quasicrystals; quasiperiodic crystals; incommensurate crystals; symmetry.

1. INTRODUCTION

The aim of this paper is to argue against the common practice⁽¹⁻⁴⁾ to restrict the definition of quasicrystals by requiring that they possess an axis of symmetry that is incompatible with periodicity. According to this restriction there are no quasicrystals in 1-dimension, and a quasicrystal in 2- or 3-dimensions must have an axis of N -fold symmetry, with $N = 5$, or $N > 6$. I propose here to accept the original definition of Levine and Steinhardt⁽⁵⁾ whereby the term *quasicrystal* is simply an abbreviation for *quasiperiodic crystal*, possibly with the proviso that the term quasicrystal be used for crystals that are strictly aperiodic (as the mathematical definition of quasiperiodicity includes periodicity as a special case).

I shall start by reviewing some basic definitions in Sec. 2. I shall then proceed in Sec. 3 to discuss the problematic distinction between the different families of quasiperiodic crystals, namely, incommensurately modulated crystals, incommensurate composite crystals, and those crystals that are

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typically referred to as quasicrystals. Finally, in Sec. 4, I shall support my call to relax the definition of quasicrystals by referring to theoretical models, as well as experimental observations, of structures which should be considered as quasicrystals even though they possess no forbidden symmetries.

2. DEFINITIONS

2.1. What Is a Crystal?

Before Shechtman's 1982 discovery of the first quasicrystal⁽⁶⁾ it was universally accepted, though never proven, that the internal order of crystals was achieved through a periodic filling of space. Crystallography treated *order* and *periodicity* synonymously, both serving equally to define the notion of a *crystal*. With that came the so-called "crystallographic restriction," stating that crystals cannot have certain forbidden symmetries, such as 5-fold rotations. The periodic nature of crystals was "confirmed" with the discovery of x-ray crystallography and numerous other experimental techniques throughout the 20th century. Periodicity became the underlying paradigm, not only for crystallography itself, but also for other disciplines such as materials science and condensed matter physics, whose most basic tools, like the Brillouin zone, rely on its existence.

Two decades later, it is now clear that periodicity and order are not synonymous, and that a decision has to be made as to which should define the term *crystal*. The International Union of Crystallography through its Commission on Aperiodic Crystals⁽⁷⁾ decided on the latter, but was not ready to give precise microscopic descriptions of all the ways in which order can be achieved. Clearly, periodicity is one way of achieving order, quasiperiodicity as in Penrose-like tilings is another, but can we be certain that there are no other ways that have not yet been discovered? The Commission opted to shift the definition from a microscopic description of the crystal to a property of the data collected in a diffraction experiment. It decided on a temporary working-definition whereby a *crystal* is "any solid having an essentially discrete diffraction diagram." Crystals that are periodic are explicitly called *periodic crystals*, all others are called *aperiodic crystals*. The new definition is consistent with the notion of long-range order, used in condensed matter physics, where the transition from a disordered liquid to an ordered solid is indicated by the appearance of an *order parameter* in the form of Bragg peaks in the diffraction diagram at non-zero wave vectors. It is sufficiently vague so as not to impose unnecessary constraints until a better understanding of crystallinity emerges. We

need not worry about this vagueness here, because we shall only be concerned with quasiperiodic crystals, which are a well defined subcategory of structures, satisfying the new definition.

2.2. What Is a Quasiperiodic Crystal?

Solids whose density functions $\rho(\mathbf{r})$ may be expanded as a superposition of a countable number of plane waves

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

are called *almost periodic crystals*. In particular, if taking integral linear combinations of a finite number D of wave vectors in this expansion can span all the rest, then the crystal is *quasiperiodic*. The diffraction pattern of a quasiperiodic crystal, therefore, contains Bragg peaks each of which can be indexed by D integers. If D is the smallest number of wave vectors that can span the whole set L using integral linear combinations then D is called the *rank*, or the *indexing dimension* of the crystals. *Periodic crystals* form a special subset of all quasiperiodic crystals whose rank D is equal to the actual physical dimension d . For periodic crystals the set of Bragg peaks is truly discrete because the set of wave vectors \mathbf{k} in their Fourier expansion (1) is discrete. For quasiperiodic crystals whose rank D is greater than the physical dimension d , the set L of wave vectors in the expansion (1) is dense—there are \mathbf{k} 's in L that cannot be surrounded by a finite d -dimensional ball that contains no other \mathbf{k} 's. Nevertheless, in actual experiments, where the total integrated diffraction intensity is finite, Bragg peaks are not observed at wave vectors \mathbf{k} for which the intensity $|\rho(\mathbf{k})|^2$ is below a certain threshold. The observed diffraction pattern is therefore essentially discrete even though the set L is not. It should be noted that all experimentally observed crystals to date are quasiperiodic.

3. THE QUASICRYSTALLOGRAPHIC RESTRICTION

Certain classes of quasiperiodic crystals were known long before Shechtman's discovery. These are the so-called *incommensurately-modulated crystals* and *incommensurate composite crystals*, (or *intergrowth compounds*). The former consist of a basic (or average) ordered structure that is perturbed periodically (modulated) in space, and the period of the modulation is incommensurate with the underlying spatial periodicities of the basic

structure.² The latter are composed of two or more interpenetrating subsystems with mutually incommensurate spatial periodicities. Each subsystem, when viewed independently, is itself a crystal which is incommensurately-modulated due to its interaction with the other subsystems. The diffraction diagrams of these special types of quasiperiodic crystals are characterized by having one or more subsets of *main reflections*—Bragg peaks that are significantly brighter than the others—describing the basic structures, and weaker peaks, called *satellites*, arising from the modulations. For more detail see, for example, Refs. 2 and 10.

Incommensurately-modulated and incommensurate composite crystals did not pose any serious challenge to the periodicity paradigm because they could all be viewed as periodic structures that had been slightly modified. Order was still obtained through periodicity—the paradigm remained intact. Shechtman's discovery implied that there exist quasiperiodic crystals for which a description in terms of a modulation of a basic periodic structure or a composition of two or more substructures is either inappropriate or impossible. Due to its forbidden 5-fold symmetry, Shechtman's quasicrystal was clearly not a quasiperiodic modification of a periodic crystal, but rather a crystal which was somehow intrinsically quasiperiodic—a crystal in which order was *not* achieved by means of periodicity. Shechtman's discovery was able to shatter the old paradigm because it was a clear violation of the crystallographic restriction. The observation of a forbidden symmetry was so pivotal in the discovery of quasicrystals that it became their defining property. The crystallographic restriction was replaced by what may be viewed as a "quasicrystallographic restriction."

It is common practice to reserve the term "quasicrystal" exclusively for those crystals, like Shechtman's, that are intrinsically quasiperiodic, setting them apart from modulated and composite crystals as a third subcategory of quasiperiodic structures. This common point of view³ is appealing for many reasons, particularly, because there are systems whose physical behavior is indeed governed by the fact that the crystal is modulated or composed of substructures. Not viewing these systems as such, and not utilizing the many theoretical and experimental tools developed specifically for treating modulated and composite crystals, would be foolish.

The problem with the desire to distinguish between intrinsically-quasiperiodic crystals and crystals in which quasiperiodicity is obtained via modulation or composition is the lack of a quantitative criterion for making this distinction. The easiest way to see the difficulty is by considering the diffraction patterns. The diffraction pattern of a modulated

² We know today of cases where the basic structure itself is already aperiodic.^(8,9)

³ See, for example, Refs. 2, 10, 11, and 12.

crystal, for example, must exhibit a subset of strong main reflections accompanied by weak satellites. This begs to ask how weak must the satellites be to be considered as such? If one could hypothetically gradually increase the intensity of the satellites and their harmonics, at what point would the structure cease to be a modulated crystal? The same difficulty can also be seen in direct space, by starting with a periodic crystal which is modulated by a smooth incommensurate sine function, and gradually increasing the amplitude of this modulation while adding higher harmonic contributions. If consequently the modulation takes the shape of an unsmooth sawtooth function would it not be more appropriate to view it as a set of separate “atomic surfaces” like one does in a quasicrystal?

It turns out that this gradual transformation of a modulated crystal into a “quasicrystal” is not at all hypothetical. There are examples of systems,⁽¹³⁾ in which this transformation happens as a function of composition. The transformed structures are described as modulated crystals, with complicated modulation functions, called “Crenel functions,”⁽¹⁴⁾ when in fact they can be described very simply as “quasicrystals” with simple atomic surfaces, as explained in Ref. 13.⁴ Although, one of the best suggestions⁽¹²⁾ for the distinction between quasicrystals and modulated crystals is based on the shape of the modulation function, it seems quite impractical as a quantitative experimental criterion.

So, even though there are clearly structures that are formed by modulating or composing simpler structures, and there are clearly other structures that are not, there is simply no quantitative criterion to distinguish between these categories of quasiperiodic structures. Unless of course, as a last resort, one adopts the quasicrystallographic restriction. The criterion is then very simple: If a quasiperiodic crystal possesses forbidden symmetries then it is a quasicrystal, otherwise it is a modulated or a composite crystal. This is probably the most appealing reason to adopt the quasicrystallographic restriction. The problem is that it leaves no room for the possible existence of crystals that are intrinsically quasiperiodic—not formed by modulation or composition—yet possess no forbidden symmetries. If such crystals cannot exist then there is no problem with adopting the quasicrystallographic restriction. If such crystals do exist then adopting the restriction would be inappropriate. So we must ask: Are there any examples of such crystals?

⁴ This may remind the reader of the famous experiment in which a group of people is shown a sequence of pictures, beginning with a cat which gradually changes into a dog. The viewers insist that they are still seeing a cat almost to the end, when in fact they are looking at a picture of a dog.

4. MANY EXAMPLES

Theoretical models of such crystals, that are intrinsically quasiperiodic yet possess no forbidden symmetries, are very easy to construct. In fact, from a theoretical standpoint it should be *obvious* that there is nothing special about point groups that are incompatible with periodicity. In principle, any method that is used to generate a quasiperiodic tiling with, say, 10-fold symmetry can be used to generate quasiperiodic tilings with, say, 4-fold symmetry. Indeed, there are many examples in the literature of tiling models of quasicrystals, with 2-, 4-, and 6-fold symmetry, generated by all the standard methods: matching rules,⁽¹⁵⁾ substitution rules,^(15,16) the cut-and-project method,^(17,18) and the dual-grid method.⁽¹⁹⁾

I have recently described the two-dimensional square Fibonacci tiling and its natural generalization into three (or even higher) dimensions.⁽²⁰⁾ It is a quasiperiodic tiling with many of the features normally associated with standard tiling models of quasicrystals like the Penrose tiling. It has a finite number of tiles with definite tile frequencies and a finite number of vertex configurations; it can be generated by most of the standard methods for generating quasiperiodic tilings; its diffraction diagram contains Bragg peaks with no clear subset of main-reflections; and most notably, it has τ -inflation symmetry, where $\tau = (1 + \sqrt{5})/2$ is the golden ratio. Like the proverbial bird that looks like a duck, walks like a duck, quacks like a duck, and is therefore a duck—the square Fibonacci tiling is a model quasicrystal even though it has no forbidden symmetries.

To the best of my knowledge, no alloys or real quasicrystals exist with the precise structure of the square or cubic Fibonacci tilings. Yet, this does not imply that structures like the square Fibonacci tiling are experimentally irrelevant. In recent years we have come to know a number of experimental applications where one creates artificial quasicrystals. One example is in the field of photonic crystals,⁽²¹⁾ with the aim of producing novel photonic band-gap materials. Another example is in field of non-linear optics,⁽²²⁾ with the aim of achieving third- and fourth-harmonic generation in a single crystal. In both of these examples it may be beneficial to make artificial quasicrystals with structures, similar to that of the square Fibonacci tiling.

The existence of theoretical models and the possibility to fabricate artificial structures might be dismissed as trivial, yet the existence of actual experimental observations is a different matter. It turns out that there have been experimental reports of quasiperiodic crystals with cubic symmetry^(23,24) as well as tetrahedral,^(25,26) tetragonal,⁽¹⁷⁾ and possibly also hexagonal⁽²⁷⁾ symmetry, that are neither modulated crystals nor composite crystals. Their diffraction diagrams show no clear subset(s) of main reflections, yet they do not possess any forbidden symmetry. One of the cubic

quasicrystals,⁽²⁴⁾ a Mg-Al alloy, is even reported to have inflation symmetry involving irrational factors related to $\sqrt{3}$. These crystals are clearly quasiperiodic yet they are not formed by modifying an underlying periodic structure. They are as intrinsically quasiperiodic as the quasicrystals that have forbidden symmetries, and should therefore all be considered quasicrystals.

5. SO, WHAT IS A QUASICRYSTAL?

I suggest that the quasicrystallographic restriction, requiring quasicrystals to possess forbidden symmetries, be officially abandoned. I would like the scientific community to accept the original definition of Levine and Steinhardt⁽⁵⁾ whereby the term *quasicrystal* is simply an abbreviation for *quasiperiodic crystal*, possibly with the proviso that the term quasicrystal be used only for crystals that are strictly aperiodic (since, as mentioned above, the mathematical definition of quasiperiodicity includes periodicity as a special case).

This paper is part of an ongoing debate on the meaning of crystallinity and the concept of a quasicrystal. Some crystallographers might still be under the impression that if a quasiperiodic crystal does not possess any forbidden symmetry it must be either an incommensurately modulated crystal or an incommensurate composite crystal, and that no other possibility exists. Many crystallographers still impose the “quasicrystallographic restriction” when defining quasicrystals in their publications. It is my firm opinion that these practices and misconceptions should be stopped, not only as a matter of academic preciseness, but more importantly, to make sure that crystallographers who discover new quasicrystals without forbidden symmetries will not hesitate to publish their findings. As we celebrate in these Journal issues the many contributions of David Mermin to science, its teaching,⁽²⁸⁾ and its communication to others,⁽²⁹⁾ a more appropriate title for this article (in the spirit of David Mermin’s “Reference Frame” columns in *Physics Today*) might have been “What’s wrong with these quasicrystals?” The answer in this case is that nothing is wrong with *these* quasicrystals—the problem lies with the definition.

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