

## Copernican Crystallography

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(Received 7 October 1991)

Crystallography is given a new formulation that abandons its traditional reliance on microscopic periodicity. Both periodic and quasiperiodic materials are treated on an equal footing by redefining the point group of a material in terms of indistinguishable (rather than identical) densities. The new paradigm is simpler and broader than the widely used "superspace" extension of the crystallographic categories to quasiperiodic materials. This is illustrated by a comparison of how the two schemes treat certain Bravais classes.

PACS numbers: 61.50.Em, 61.42.+h

Microscopic periodicity underlies the classification scheme of crystallography, begun 150 years ago with Frankenheim and Bravais's enumeration of the classes of crystal lattices [1]. By the time quasiperiodic materials were discovered—incommensurately modulated crystals a few decades ago and quasicrystals within the last decade—periodicity had become so enshrined as the *sine qua non* of the crystallographers' taxonomy that the extension to quasiperiodic materials was achieved only by expressing them as three-dimensional sections of materials periodic in more than three dimensions, to which the higher-dimensional crystallography of periodic materials could be applied. In this Letter I argue that this ascent into superspace in search of periodicity leads to a crystallographic scheme which is excessively complicated and potentially misleading. A simpler and unified scheme for the classification of both periodic and quasiperiodic materials can be formulated and constructed without ever leaving three dimensions.

Quasiperiodic materials lack perfect translational symmetry but have the property—reminiscent of but weaker than periodicity—that given any subregion, a translation can be found through a distance of the order of its dimensions that takes the subregion into an identical one. Although not often emphasized, there is an analogous weakening of rotational symmetry: The image under appropriate rotations of any region of certain quasiperiodic materials can also be found in the unrotated material at a distance of the order of the dimensions of the region. Periodic materials possess these properties in a much stronger form: The required translation can be through a microscopic distance, independent of the size of the subregion, and the coincidence with the original material is not confined to a subregion, but is perfect.

The essential character of these quasisymmetries is precisely captured in the concept of *indistinguishable*, as opposed to *identical*, densities. Two densities are indistinguishable if any substructure on any scale that occurs in one occurs in the other with the same frequency. Putting it analytically, two densities are indistinguishable if their positionally averaged  $n$ -point autocorrelation functions are the same for all  $n$ . Two *periodic* densities can be indistinguishable only if they differ by at most a transla-

tion, but two indistinguishable *quasiperiodic* densities need not be so simply related. The key to reformulating crystallography without requiring periodicity is this: One defines the *point group* of a material to be the set of operations from  $O(3)$  that take the density into one that is *indistinguishable from* the original.

Should a material happen to be periodic so that indistinguishability reduces to identity to within a translation, then one can combine the point-group operations with such translations, arriving at the conventional classification in terms of subgroups (the crystallographic space groups) of the real-space Euclidean group that leave the material *identical* to what it was. Should the material be quasiperiodic, however, translations cease to be relevant: Since indistinguishability is based on *positionally averaged* correlation functions, an operation in its point group leaves a material indistinguishable regardless of the origin about which it is applied. Basing the point group on indistinguishability might thus appear to entail the loss of some important additional structure, but that structure can be recovered in the quasiperiodic case and usefully reformulated in the periodic case by noting that the most analytically straightforward definition of both quasiperiodicity and indistinguishability of densities is to be found in Fourier space.

Densities of quasiperiodic materials are defined to be superpositions of plane waves whose wave vectors can be expressed as a lattice [2] of integral linear combinations of  $3+d$  primitive wave vectors that span a three-dimensional space and are linearly independent over the integers. A material is quasiperiodic if  $d > 0$  and merely periodic if  $d = 0$ . Two densities are indistinguishable if and only if the products of their Fourier coefficients over any set of wave vectors summing to zero always agree. When combined with the definition that a point-group operation leaves the density indistinguishable, this leads straightforwardly to a classification scheme, valid for periodic or quasiperiodic materials, that is based on the point group and the phase relations between density Fourier coefficients at wave vectors connected by point-group operations [3,4].

The virtues of Fourier space, even as the venue for the traditional crystallography of periodic materials, were

celebrated by Bienenstock and Ewald [5] three decades ago. They pointed out that the 230 crystallographic categories of Schönflies, Fedorov, and Barlow could be derived simply and efficiently in Fourier space as classes of phase relations between density Fourier coefficients at wave vectors related by point-group operations. Quasiperiodic materials not then having attracted serious attention, Bienenstock and Ewald presented their method only as an alternative approach to the ordinary crystallography of periodic materials. But when the formulation of crystallography is freed from its traditional reliance on periodicity, their Fourier-space classification scheme emerges unavoidably as the natural way to organize the broader class of quasiperiodic materials.

This broader organization continues to use the crystallographic concept of Bravais class. While the Bravais classes of conventional crystallography are usually viewed as classes of lattices of translations that express the real-space periodicity of the crystal, there is an alternative view of the lattices in a Bravais class which continues to make perfect sense for quasiperiodic materials. A (reciprocal) lattice is the closure under subtraction of the set of all wave vectors at which the density has nonvanishing Fourier coefficients. These are the lattices of most immediate concern from the point of view of diffraction, being directly deducible from the observed Bragg peaks by application of the familiar Laue rules. In the crystallographic case two lattices with the same point group [6] are in the same Bravais class if it is possible to interpolate [7] between them through a family of lattices all of which have that point group. In the quasiperiodic extension of the concept of Bravais class, the lattices of wave vectors in the family interpolating between two  $3+d$  lattices should in addition have the same  $d$ .

Reference [4] spells out the procedure by which one calculates the finer subclassifications of materials with a given point group and Bravais class (which are the space groups in the periodic case), applying the method to a unified treatment of both crystals and quasicrystals. Here I shall show how a scheme based on indistinguishable densities differs from the superspace scheme by comparing how they each describe a particular class of incommensurately modulated crystals. Surprisingly, the two schemes lead to different categories. The artifact of superspace turns out to be built into the current classification of incommensurately modulated crystals, henceforth designated as the JJdW scheme [8]. As a result the unambiguous applicability of the scheme is limited to materials whose diffraction patterns reveal a particular subset of strong peaks (a "lattice of main reflections") that can be associated with a crystallographic lattice in ordinary three-dimensional space, the remaining weaker peaks ("satellites") having nonzero components in the  $d$ -additional superspace dimensions.

This state of affairs shows up even at the rudimentary level of Bravais class, where it can be illustrated by examining the Bravais classes for the simplest quasiperiodic

materials with point groups from the cubic crystal system. These Bravais classes contain lattices of three-dimensional wave vectors that can be represented as integral linear combinations of six integrally independent vectors, with a symmetry group which is either the full cubic group  $m3m$  or the full tetrahedral group  $m3$ . A detailed computation of the  $(3+3)$  cubic Bravais classes has been given elsewhere [9]. Using the fact that a cubic  $(3+3)$  lattice must have at least the symmetries in  $m3$  one easily establishes that it can be viewed as a set of integral linear combinations of six vectors constituting an orthonormal triad, and a second triad, identically oriented but rescaled by an incommensurate factor. One also establishes that the set contains *all* vectors with even indices, so that a general lattice can be specified by listing the finite set of vectors indexed only by 1's or 0's, the full lattice consisting of the sums of these vectors with all vectors of the even sublattice. Since such finite sets must themselves have cubic symmetry, and be closed under addition modulo 2, they are readily enumerated, and yield just nine distinct Bravais classes.

These nine Bravais classes are listed in Table I. The six with symmetry group  $m3m$  contain lattices given by the sums of all pairs of vectors from two ordinary crystallographic lattices, identically oriented but incommensurately scaled, each of which can be from either the crystallographic  $P$ ,  $F^*$ , or  $I^*$  Bravais class [10]. In addition, there are three Bravais classes with only tetrahedral symmetry. The simplest of these,  $T_0$ , consists of the even sublattice and the sums of its vectors with the three indexed by  $[101,011]$ ,  $[110,101]$ , and  $[011,110]$ . A lattice from the Bravais class  $T_1$  is given by a  $T_0$  lattice and the

TABLE I. The nine  $(3+3)$  cubic Bravais classes. The JJdW symbols and numbers are given in the second column and, when a class of lattices of three-dimensional wave vectors occurs under more than one name in their catalog, in the third and fourth (in curly brackets, to emphasize the redundancy). The designation  $P+I^*$  could equally well be taken to be  $I^*+P$ ; the order is immaterial (and similarly for  $P+F^*$  and  $F^*+I^*$ ). For appropriate values of the incommensuration parameter, the tetrahedral  $T_0$ ,  $T_1$  (in either of its JJdW manifestations), and  $T_2$  lattices acquire icosahedral symmetry and become the quasicrystallographic icosahedral  $F^*$ ,  $P$ , and  $I^*$  lattices, respectively.

Cubic			
$P + P$	$Pm3m(\alpha 00)$	208	
$I^* + I^*$	$Fm3m(\alpha \alpha \alpha)$	217	
$F^* + F^*$	$Im3m(0\beta\beta)$	219	
$P + I^*$	$Pm3m(\alpha \alpha \alpha)$	215	{ $Fm3m(\alpha 00)$ 211 }
$P + F^*$	$Pm3m(0\beta\beta)$	212	{ $Im3m(\alpha 00)$ 210 }
$F^* + I^*$	$Im3m(\alpha \alpha \alpha)$	216	{ $Fm3m(0\beta\beta)$ 214 } { $Pm3m(\alpha \frac{1}{2} \frac{1}{2})$ 209 }
Tetrahedral			
$T_0$	$Pm3(\frac{1}{2}\beta\beta + \frac{1}{2})$	206	
$T_1$	$Fm3(1\beta\beta + 1)$	207	{ $Pm3(\alpha \frac{1}{2} 0)$ 204 }
$T_2$	$Fm3(\alpha 10)$	205	

sums of its vectors with  $[111,000]$ , while a lattice from  $T_2$  is given by a  $T_0$  lattice and the sums of its vectors with  $[111,000]$ ,  $[000,111]$ , and  $[111,111]$ . One readily verifies that these nine Bravais classes are distinct and contain lattices of the appropriate symmetry. Reference [9] establishes that there are no other 3+3 Bravais classes with symmetry groups  $m\bar{3}m$  or  $m\bar{3}$ .

The JJdW classification scheme derives the 3+3 cubic Bravais classes in quite a different manner. One starts with a crystallographic lattice from one of the three crystallographic Bravais classes (the lattice of main reflections) and an incommensurate modulation vector, whose images under the group  $m\bar{3}m$  or  $m\bar{3}$ , together with the crystallographic lattice, generate a 3+3 lattice (called a "Z module" by JJdW). One thus introduces at the start an asymmetry between vectors associated with a crystallographic lattice and vectors arising from an incommensurate modulation. The Bravais classes one subsequently arrives at are identical to the nine described above, but they now arise in various guises, depending on which rank-3 crystallographic sublattice one happens to single out as the lattice of main reflections. These various ways of describing one and the same set of three-dimensional wave vectors are treated in the JJdW scheme as distinct Bravais classes, labeled by the conventional crystallographic designation for the lattice of main reflections followed by a specification of the modulation vector, as indicated in Table I.

The redundancy (in terms of three-dimensional wave vectors) of the JJdW scheme is particularly evident in the case of the  $P+I^*$  and  $P+F^*$  Bravais classes, each of which appears in two guises depending on which crystallographic sublattice is taken to be the lattice of main reflections and which describes the enrichment of the lattice of main reflections by the modulation vectors. The appearance of  $F^*+I^*$  in the JJdW scheme is further complicated by the presence of a third ( $P$ ) crystallographic sublattice. The tetrahedral Bravais class  $T_1$  also has two representations as a lattice of main reflections and satellites, which are treated by JJdW as distinct Bravais classes.

One might argue that the redundant JJdW Bravais categories should be maintained as distinct Bravais classes in spite of their identity as classes of lattices of three-dimensional wave vectors, because most currently known incommensurately modulated crystals are clearly best described by a particular one of the redundant forms. Thus an ordinary crystal with a primitive cubic lattice can undergo a displacive phase transition characterized by frozen-in phonons along  $[111]$  directions, ending up in JJdW's class  $Pm\bar{3}m(aaa)$ , while a crystal with a real-space  $F$  lattice with frozen-in  $[100]$  phonons would be in their  $Fm\bar{3}m(a00)$  class. We, however, would place both materials in the single Bravais class  $P+I^*$ , even though they arise in very different ways and are easily distinguished. For although this distinction is important, it ought not to be made at the level of Bravais class, as

the superspace approach induces one to do.

The problem with the JJdW scheme is that the Bravais class of a material is no longer determined by the Fourier-space locations of the Bragg peaks, as it is in the periodic crystallographic case; one requires, in addition, information about the relative peak intensities beyond what symmetry requires, since the lattice of main reflections is identified from the strongest peaks. But there are sound reasons for keeping peak intensities out of as fundamental a notion as Bravais class. If the Bravais class can change with the peak intensities, one must introduce questions of degree into a concept otherwise based entirely on symmetry: How much stronger do certain peaks have to be for the determination to be unambiguous? Putting it another way, one can specify a family of densities that interpolate between the two Bravais classes without any change in point group or rank [11]. One can avoid an arbitrary boundary between Bravais classes by excluding intermediate materials from the domain of applicability of the scheme, but since materials exist (quasicrystals, incommensurate intergrowth compounds) whose diffraction patterns reveal no hint of a lattice of main reflections, one is then required to impose a distinct crystallography on such materials, when a perfectly satisfactory scheme already exists.

For those materials that do admit a lattice of main reflections, it is obviously important to *supplement* the specification of the Bravais class with a statement of which of the possible crystallographic sublattices contains the strong peaks. Ordinary crystallography offers many analogies. Consider, for example, a cubic crystal which undergoes a uniaxial compression to tetragonal (which could be viewed as a frozen-in  $\mathbf{k}=0$  phonon). There is a clear and important difference between slightly compressed face-centered-cubic or body-centered-cubic crystals. But the compressed crystals both belong to the single centered-tetragonal Bravais class. One would not build this difference into the concept of Bravais class with a special reformulation of crystallography containing two versions of the centered-tetragonal class, restricted in application to nearly cubic materials.

The sole advantage of searching in superspace for a classification scheme based on periodicity is that it relieves one of having to take a radical new look at the foundations of ordinary crystallography. The disadvantages are displayed in Table I. A celebrated analogy comes to mind. If the Sun were the only thing of interest in the heavens, it would be foolish not to regard it as moving around the Earth. Because this view became firmly entrenched, generations of astronomers had to become adept at manipulating epicycles to account for the motions of the planets. While it was wrenching to shift to a heliocentric perspective, the eventual simplification in the more broadly applied scheme more than made up for the pain of abandoning the Ptolemaic view. When all materials of interest were periodic, a crystallography based on periodicity grew and thrived. Epicycles began

to proliferate, in the form of superspace groups, when the scheme was extended to quasiperiodic materials without abandoning its conceptual reliance on periodicity. While unwilling to burn for it at the stake, I would like to suggest that others could spare themselves significant pain by abandoning Ptolemaic crystallography and learning how to classify both periodic and quasiperiodic materials, not by ascending to superspace in search of periodicity, but by resting the foundations of crystallography on the three-dimensional concept of a point group of operations that change the density into something indistinguishable.

My appreciation for the power of a theory of symmetry based on indistinguishable densities developed during many collaborations with Daniel Rokhsar, David Wright, Jason Ho, and David Rabson. I am indebted to Ron Lifshitz for joining me in a three-dimensional derivation of JdW Bravais classes, and to Sander van Smaalen and Ted Janssen, whose thoughtful responses to that derivation led me to wonder whether crystallography might be in need of a paradigm shift. Veit Elser, Chris Henley, Leonid Levitov, and Michael Widom commented helpfully on earlier versions of the manuscript. This research is supported by the National Science Foundation, Grant No. DMR 8920979.

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[1] Bravais (1848) pointed out that two of the 15 classes of Frankenheim (1842) were identical. See A.E.H. Tutton, *Crystallography and Practical Crystal Measurement* (MacMillan, London, 1922).

[2] A countable set of vectors is a lattice if  $\mathbf{v}-\mathbf{w}$  is in the set whenever  $\mathbf{v}$  and  $\mathbf{w}$  are. The minimum number,  $3+d$ , of

vectors whose integral linear combinations include all lattice vectors is called the *rank* of the lattice.

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- [4] D. A. Rabson, N. D. Mermin, D. S. Rokhsar, and D. C. Wright, *Rev. Mod. Phys.* **63**, 699 (1991); N. D. Mermin, *Rev. Mod. Phys.* **64**, 3 (1992).
- [5] A. Bienenstock and P. P. Ewald, *Acta Crystallogr.* **15**, 1253 (1962).
- [6] When applied to lattices, we use the term "point group" in its traditional sense: Lattices associated with periodic or quasiperiodic materials are invariant under their point-group operations, which are applied about the origin of Fourier space. As in conventional crystallography, the point group of the associated material, in the new generalized sense introduced above, is a subgroup of the point group of its lattice.
- [7] Members of an *interpolating* family can be taken arbitrarily close together; a *continuous* family might necessarily contain lattices with accidentally larger point groups or with accidentally commensurate generating vectors. An interpolating family can avoid such special cases with arbitrarily small gaps.
- [8] P. M. de Wolff, T. Janssen, and A. Janner, *Acta Crystallogr., Sect. A* **37**, 625 (1981); A. Janner, T. Janssen, and P. M. de Wolff, *Acta Crystallogr., Sect. A* **39**, 658 (1983); **39**, 667 (1983); **39**, 671 (1983).
- [9] N. D. Mermin and R. Lifshitz, *Acta Crystallogr., Sect. A* (to be published).
- [10] Since the lattices contain wave vectors, they are better labeled by their structure in reciprocal space (\*). Thus a crystallographic  $F^*$  lattice, more conventionally denoted by  $I$ , is face centered in reciprocal space.
- [11] It may not be possible to achieve such an interpolation through densities that represent well-localized particles, but a crystallographic classification scheme ought to be powerful enough to embrace the "softer" kinds of densities found, for example, in certain liquid crystals.