Structural Analysis of Aperiodic Crystals

Workshop No. 4

at the XX Congress of the IUCr

23 August 2005

Florence, Italy

Workshop Structural Analysis of Aperiodic Crystals
23 August 2005
at the XX Congress of the IUCr in Florence.

The Workshop **Structural Analysis of Aperiodic Crystals** is intended to give an overview of the state of the art of crystallographic analysis of incommensurately modulated crystals, incommensurate composite crystals, polytypes and quasicrystals. Introductory lectures will present the basic phenomena related to aperiodic order, including diffraction and morphology, and the fundamental principles of the superspace descriptions of their crystal structures. The afternoon session will be devoted to recent developments and applications of superspace crystallography.

Organized on behalf of the Commission on Aperiodic Crystals of the IUCr by

Sander van Smaalen[1] and Ray L. Withers[2]

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Program

8.30 – 9.30		*Registration*
9.30 – 9.35	S. van Smaalen	*Opening remarks*
9.35 – 10.30	W. Steurer	Quasicrystals
10.30 – 11.00		*Coffee break*
11.00 – 11.45	G. Chapuis	Superspace description of modulated structures
11.45 – 12.30	A. Schönleber	Introduction to superspace symmetry
12.30 – 14.00		*Lunch*
14.00 – 14.30	S. Lidin	Incommensurate structural refinements from powder data—The symmetry point of view
14.30 – 15.00	B. Toudic	Superspace symmetry breakings in aperiodic molecular nanoporous crystals
15.00 – 15.30	O. Perez	Modulations as "a vector" for crystal order and non stoichiometry in layered oxides
15.30 – 16.00	R. Lifshitz	Symmetry of aperiodic crystals
16.00 – 16.15	R. Withers	*Closing remarks*
18.00		*Start of the XX Congress of the IUCr*

Aperiodic crystals at the XX Congress of the IUCr.

23 AUG Tuesday	8.30 – 16.10	Workshop No.4 – Aperiodic Crystals
25 AUG Thursday	8.30 – 9.30	Keynote lecture KN7 by V. Petricek: *Structure Analysis of Modulated Crystals: Trends and Tendencies* (Chair: R. Withers).
	10.00 – 12.35	Microsymposium MS19, *News from incommensurate structures.* Speakers: D. Fredrickson, J.M. Perez-Mato, R. Withers, Y. Michiue and G. Borgstahl. (Chairs: S. van Smaalen and S. Lidin.)
	14.45 – 17.20	Microsymposium MS26, *Recent advances in quasicrystal research.* Speakers: R. Mc-Grath, Z. Papadopolos, M. de Boissieu, G. Krauss and Y. Matsushita. (Chairs: K. Saitoh and R. Lifshitz.)
	17.30 – 18.30	Keynote lecture KN10 by A. Yamamoto: *Quasicrystal Structure Analysis. The State of the Art* (Chair: M. De Boissieu).
29 AUG Monday	14.45 – 17.20	Microsymposium MS83, *Computational solutions for aperiodic crystals.* Speakers: M. Dusek, S. van Smaalen, L. Palatinus, Z. Izaola and I. Orlov. (Chairs: Ch. Svensson and V. Favre-Nicolin.)

Aperiodic 2006 (Aperiodic'06)

18-22, September 2006
Zao, Miyagi, Japan

The "Aperiodic'06" will be held at the Miyagi Zao Royal Hotel in Zao, Miyagi, Japan from 18 to 22, September, 2006. Miyagi Zao Royal Hotel

Topics

Mathematics of aperiodic crystals, Theoretical studies on aperiodic crystals, Crystallography, Structures, Defects, diffuse scattering, Morphology and Growth, Phase transitions,, Phonons and Phasons, Properties, Interfaces and Surfaces,, Applications.

Location

Zao is in Miyagi prefecture and located near Sendai, the largest city in the northern part of the main island of Japan. Sendai is accessible by airplane and super-express train (shinkansen). It takes about one hour by bus from Sendai. The shuttle bus will be available.

Call for Papers

Contributions on the above topics are invited for oral and poster presentations at the conference. The online registration and submission of abstracts will become available by the end of 2005.

Conference Publications

An Abstract Book will be provided for delegates at the conference. Selected papers will be published in a Special Issue of Philosophical Magazine.

Conference Chairpersons: A. Yamamoto and A. P. Tsai
Conference Secretary: S. Fujimoto
Organizing Committee: A. Yamamoto, A. P. Tsai, K. Saitoh, Y. Gotoh, Y. Miyazaki, Y. Michiue
Local Organizing Committee: S. Kameoka, K. Tsuda, S. Ohhashi
Program Committee: T. Ishimasa, T. J. Sato, H. Takakura, M. Onoda, M. Isobe, J. Morita
International Advisory Board: S. van Smaalen (Germany), G. Chapuis(Switzerland), R. L. Withers (Australia), J. M. Perez-Mato (Spain), D. Pandey (India), M. Widom (USA), M. de Boissieu (France), W. Steurer (Switzerland), K. Niizeki (Japan), R. McGrath (UK), S. Lidin (Sweden)

For further information, please visit the following web site
http://aperiodic01.tagen.tohoku.ac.jp/index.html

5th Workshop on Structural Analysis of Aperiodic Crystals

March 2007 at the University of Bayreuth, Germany

Mission Statement

The 5th Workshop on Structural Analysis of Aperiodic Crystals continues a series of workshops on the structure determination of incommensurately modulated crystals and composite crystals at the University of Bayreuth. Purpose is to present an overview of the methods of structure determination and structural analysis of incommensurately modulated structures and composite crystals. Lectures will cover the basic principles of the superspace description of modulated structures as well as advanced topics and recent developments. In addition to the series of lectures the participants will have the opportunity to practice structure refinements using the computer program JANA2000 (written by V. Petricek, M. Dusek and L. Palatinus, Prague). A step-by-step tutorial with several examples will be provided, but your own data sets are welcome, too.

Confirmed
speakers: V. Petricek (Prague), A. Schönleber and S. van Smaalen (Bayreuth).
Dates: Three days in March 2007.
Venue: Campus of the University of Bayreuth, Bayreuth, Germany.
Support: Limited funds are available for the support of young scientists.
Scientific contributions: Participants are cordially invited to submit an abstract (one page A4 paper, 12 point Times font) for a presentation of their scientific results.

Organised on behalf of the Commission on Aperiodic Crystals of the German Crystallographic Association (DGK) by Prof. Sander van Smaalen, Laboratory of Crystallography, University of Bayreuth, D-95440 Bayreuth, Germany.
Contact Email: smash@uni-bayreuth.de
Homepage: http://www.uni-bayreuth.de/departments/crystal/inc-workshop2007/index.html

Disclaimer: There is a maximum number of participants. The workshop will take place only, if a minimum of 8 participants is reached.

Workshop Structural Analysis of Aperiodic Crystals
on **23 August 2005 at the XX Congress of the IUCr in Florence.**
Organized by Sander van Smaalen and Ray L. Withers.

Abstracts

Crystallography of quasicrystals

Walter Steurer

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The structure analysis of quasicrystals is still a highly non-trivial task [1]. In conventional structure analysis the translational periodicity of the structure is taken for granted. Therefore, only the structure of a single unit cell has to be determined. In the case of quasicrystals, both the local structure of the basic structural units ('clusters') as well as their kind of long-range ordering have to be unravelled. Rational approximants, *i.e.* periodic structures built from the same clusters as quasicrystals, provide easy access to the local structure of quasicrystals. However, finding the way the clusters are arranged on the long scale is still a major problem. While three-dimensional (3D) periodic structures can be described based on just 14 Bravais lattices, the number of 'quasilattices' (tilings) of 3D quasiperiodic structures is infinite.

In the framework of the nD approach, each quasilattice results from the intersection of a nD periodic hyper-crystal structure by the 3D physical space (Fig. 1). The kind of quasiperiodic long-range order depends on nD space-group symmetry and shape of the (n-3)D 'atomic surfaces' ('occupation domains'). The nD approach allows to use many of the tools of standard structure analysis, such as the Patterson function, in a modified manner.

In the talk, the crystallographic description of decagonal and icosahedral quasicrystals [2] will be introduced and illustrated with several examples.
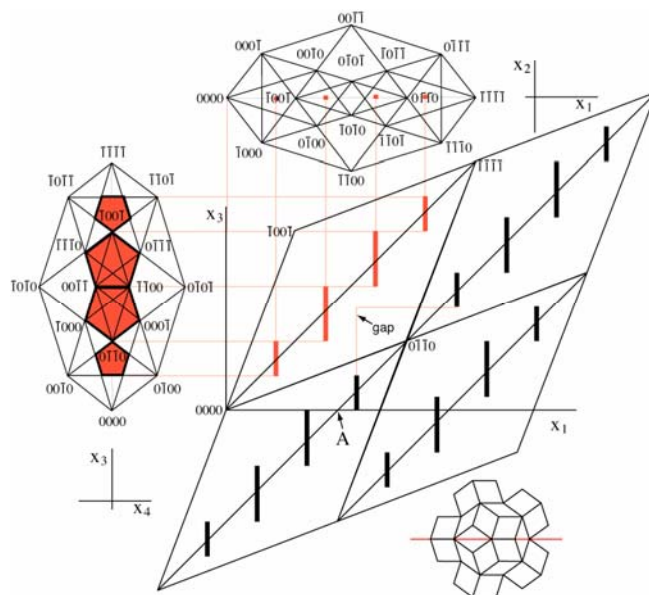

Figure 1. Characteristic $(1001)_V$ section of the Penrose tiling together with the parallel- and perpendicular-space projections of one 4D unit cell onto $(1100)_V$ and $(0011)_V$, respectively.

[1] W. Steurer, J. Non-Cryst. Solids **334 & 335**, 137-142 (2004).
[2] W. Steurer and T. Haibach, *International Tables for Crystallography*. Vol. **B**, Ed. U. Shmueli, Kluwer Academic Publishers, Dordrecht, 486-518 (2001).

Superspace description of modulated structures

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Historically, the concept of modulated structures is closely associated with the structure of γ-Na_2CO_3 which in the seventies resisted any attempt for a precise structural analysis. The appearance of additional reflections surrounding the main reflections was noted on single crystal diffractograms. Their positions were however not compatible with any reciprocal lattice periodicity and were therefore called satellite reflections owing to their properties of being linked to main reflections rather than to a lattice encompassing the full spectrum of reflections. It was the merit of P.M. de Wolff [1] to interpret this peculiar diffraction pattern as a three dimensional projection of a higher dimensional reciprocal lattice, an idea which led directly to the generalisation of the concept of a crystal. This generalisation consisted in using more then three integers to fully characterise each individual diffraction peak. The corollary was then to develop a theory of periodic crystals in spaces of higher dimension, *i.e.* the superspace in order to deal with the new experimental observations. The framework was thus established in order to describe the structures of incommensurately modulated crystals. Later, a new class of materials called composite crystals and still later, the discovery of quasicrystals only reinforced the validity of the superspace concept to describe any material requiring more than three integers to index their diffraction pattern. Currently, the concept of *aperiodic crystals* is systematically used to reunite these families under a common denominator.

What is the essence of superspace to describe crystalline structures? Any crystal structure requiring more than three integers to index its diffraction pattern can be described as a periodic object in a superspace with a dimension equal to the number of required integers. The structure observed in our real word is a three dimensional cut of this superspace. In general this cut is irrational and consequently the crystal is aperiodic. γ-Na_2CO_3 is an example of an aperiodic crystal. Rational cuts are also possible. In this case, the structure is periodic and is usually called a superstructure.

In dealing with aperiodic structures, the challenge for the crystallographer is to find an adequate description of the shape function describing the position of atoms in higher dimensions. Many efforts have been invested in the past in order to find the most appropriate functions for the description of aperiodic crystals. Presently, good software tools are available for the refinement of aperiodic structures and improvements are constantly brought up.

In the last few years however, many interesting properties of the superspace concept have been discovered which are directly applicable to conventional crystals. Currently, this concept is often adopted for the description of pressure or temperature dependent series of phases. The same concept appears also to be very useful for the description of modular structures, *i.e.* families of structures based on a small number of building blocks like ferrites or Aurivillius phases. This field is apparently in full development and many new applications can be expected in the nearest future.

[1] P.M. de Wolff, Acta Cryst. **A 30**, 777-785 (1974).

Introduction to superspace symmetry

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The concept of symmetry is fundamental to crystallography, such that the description of any structure is essentially based on its space group symmetry. The identification of its space group is a prerequisite for the solution of a crystal structure.

Aperiodic crystals (incommensurately modulated structures, composite structures, quasicrystals) do not possess three-dimensional translational symmetry, but they have long-range order. The latter corresponds to sharp Bragg reflections in the diffraction patterns. This long range order can be expressed in terms of symmetry by applying the superspace formalism via superspace groups. The crystal structure will be embedded into superspace to recover translational symmetry (Figure 1). The superspace groups are $(3+d)$-dimensional space groups with additional properties (in comparison to general higher-dimensional space groups) because of the privileged role of the three-dimensional physical subspace V_E with respect to the additional d-dimensional subspace V_I. For the particular case of one-dimensionally modulated structures, *i.e.* structures for which all the diffraction vectors can be described by four integers *hklm*, the full set of $(3+1)$-dimensional superspace groups has been tabulated [1].

Similar to the three-dimensional space groups, the superspace group can be selected on the basis of selection rules characterized by systematic absences in the diffracted intensities (main as well as satellite reflections, see Figure 2).
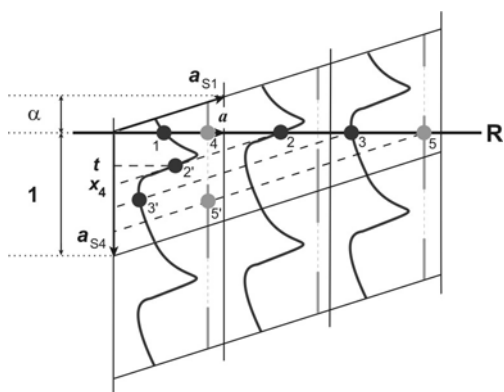

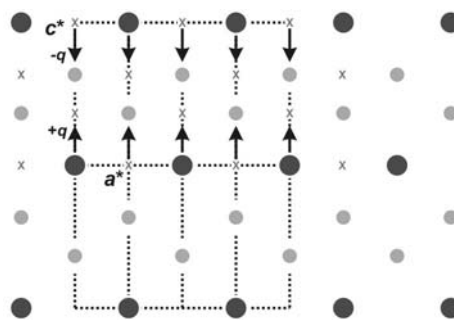*Figure 1: Schematic presentation of the embedding of a crystal structure into superspace.*

Figure 2: Schematic view of systematic absences (x) of main (●) and satellite (○) reflections.

The general principles of superspace symmetry will be discussed. Some examples will be presented, that illustrate the elegance of the superspace approach and the use of superspace groups in structural analysis of modulated crystals.

[1] T. Janssen, A. Janner, A. Looijenga-Vos, P. M. de Wolff, in A. J. C. Wilson, E. Prince (eds.) *International   Tables   for   Crystallography - Volume C*, Kluwer Academic Publishers, Dordrecht, pp. 899–937 (1999).

Incommensurate structural refinements from powder data – The symmetry point of view

B. Malaman,[1] G. Venturini,[1] J. Christensen,[2] and <u>S. Lidin</u>[2]

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Normally the symmetry of an incommensurate phase is determined from the symmetry and extinction conditions of the diffraction pattern, but in some cases it is more useful to consider the symmetries of known, related, commensurate phases. In this talk we will discuss three families of incommensurate structures; the system $ScFe_6Ge_{6-x}Ga_x$ [1], systems based on the $ThSi_2$ type structure [2,3] and systems based on defect AlB_2 type structures [4,5]. The first family of compounds constitutes a more or less continuous series of compounds ranging from the pure germanium compound that crystallizes in space group Cmmm in the $HfFe_6Ge_6$ type structure to the pure gallium compound crystallizing in the space group Immm. The intermediate compositions form a range of intergrowths between the two parent structures that is modelled very simply by an incommensurate approach in the superspace group Xmmm(0b0) and a sub-group of this, X2/m(ab0).

The second family of compounds consists of a large family of sub-stoichiometric early rare-earth digermanides. The basic structure crystallizes in the space group Fddd and the incommensurate family belongs to the superspace group Fddd(0b0)s00.

The third and final family of compounds are sub-stoichiometric late rare-earth digermanides adopting a defect AlB_2 structure (Fig. 1). The parent structure is hexagonal with the space group P6/mmm, while the modulated structures crystallize in the superspace group X2/m(a0g)0s.

For all families single cases were studied, and the structures were refined from powder samples. Once the approximate cell parameters where determined, refinement was simple and convergence rapid.
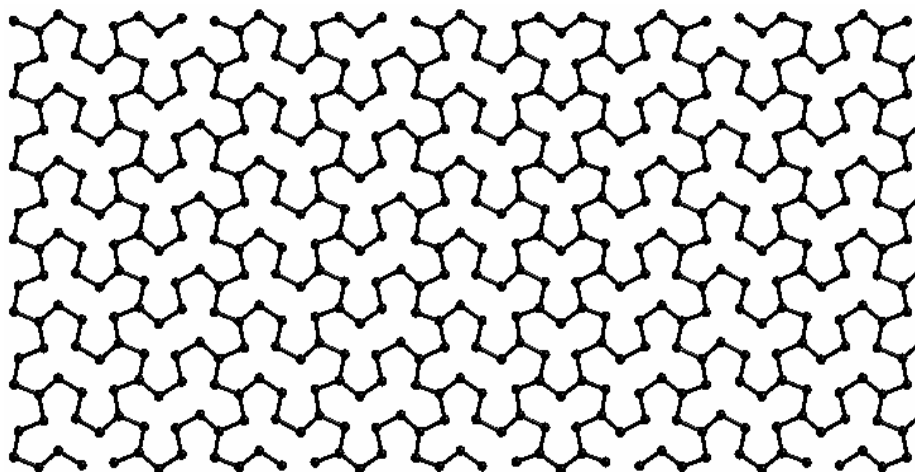

Fig. 1. Ge-substructure of a defect AlB_2 type compound.

[1] G. Venturini, J. Alloys and Compounds **322**, 190-197 (2001).
[2] G. Venturini, I. Ijjaali and B. Malaman, J. Alloys and Compounds **289**, 168-177 (1999).
[3] G. Venturini, I. Ijjaali and B. Malaman, J. Alloys and Compounds **285**, 194-203 (1999).
[4] G. Venturini, A. Verniere and B. Malaman, J. Alloys and Compounds **291**, 201-207 (1999).
[5] G. Venturini, I. Ijjaali and B. Malaman, J. Alloys and Compounds **284**, 262-269 (1999).

Superspace symmetry breakings in aperiodic molecular nanoporous crystals

B. Toudic[1], P. Rabiller[1], C. Odin[1], C. Ecolivet[1], P. Garcia[1], F. Le Gac[1], L. Bourgeois[1,2], P. Bourges[2] and T. Brewczewski[3]

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Supramolecular chemistry has opened a broad field of investigation to solid state physicists by its ability to produce new self-assembled materials. A prototype tubular example of self-organization is given by inclusion crystals, such as urea nanoporous compounds [1,2]. This simple paradigm crystal offers a unique opportunity to address at a fundamental level the question of the nature of interactions in self-organized architectures [3,4].

Many intergrowth materials are aperiodic by construction and their structures are then described in the framework of superspace crystallography [5,6]. It is well-known that aperiodicity allows original features considering the specific collective dynamics. Another case, where the additional degrees of freedom given by superspace crystallography may play a fundamental role, concerns structural phase transitions. Here, we will present new evidence of pure symmetry breaking in a superspace, together with all other types of transitions allowed with such degrees of freedom. Unexpected information concerning the actual interactions in these organic host-guest compounds comes out of these results.

[1] M.D. Hollingsworth and K.D.M. Harris, in *Comprehensive Supramolecular Chemistry Vol. 6*, edited by D.D. MacNicol, F. Toda and R. Bishop (Pergamon Press, New York, 1996) pp. 177-267.
[2] R. Lefort, J. Etrillard, B. Toudic, F. Guillaume,T. Breczewski and P. Bourges, Phys. Rev. Lett. **77**, 4027-4031 (1996).
[3] L. Bourgeois, C. Ecolivet, B. Toudic, P. Bourges, T. Breczewski, Phys. Rev. Lett. **91**, 25504 (2003).
[4] L. Bourgeois, B. Toudic, C. Ecolivet, J.C. Ameline, P. Bourges, T. Breczewski, F. Guillaume, Phys. Rev. Lett. **93**, 26101 (2004).
[5] T. Janssen, A. Janner, A. Looijenga-Vos, and P.M. de Wolff, in *International Tables for Crystallography Vol. C*, edited by A.J.C. Wilson (Kluwer, Dordrecht, 1995) pp. 797-844.
[6] S. van Smaalen and K.D.M. Harris, Proc. Roy. Soc. London A **452**, 677-700 (1996).

Modulations as "a vector" for crystal order and non stoichiometry in layered oxides

O. Pérez, B. Mellenne, C. Lepoittevin, D. Grebille, D. Pelloquin, R. Retoux, S. Malo and M. Hervieu,

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$Sr_2Ga_{2/3}Co_{7/3}O_{6+\delta}$ and $Sr_2Fe_3O_{6+\delta}$ [1] belong to the Ruddelsen-Popper family and are related to the high-T_c superconductor oxide $Bi_2Sr_2CuO_{6+\delta}$ [2]. These layered phases exhibit commensurate and incommensurate modulations. The general expression for the modulation wave vector is $\mathbf{q} = \alpha\mathbf{a^*}+\gamma\mathbf{c^*}$; α varies with the oxygen rate *i.e.* with δ. The symmetry of $Sr_2Ga_{2/3}Co_{7/3}O_{6+\delta}$ and $Sr_2Fe_3O_{6+\delta}$ can be described using the superspace formalism [3] by the same superspace group Amaa(α01). The cases corresponding to α = 1/3, 2/7 and 0.46 were investigated but other α values were also observed. Similar models were obtained; they reveal the existence of a strong and linear displacive modulation within the [MO] layers (M = Fe or Co). Extra oxygen atoms were located for a limited x_4 interval in these layers; they were modeled using crenel functions. For the commensurate cases both the superspace approach, including the analysis of 3D sections, and the classical superstructure treatment were performed; the complex model developed for the [MO] layers combining sawtooth and crenel functions is then validated. The incommensurate case provided accurate (3+1)D Fourier maps and highlighted the existence of residual static disorder in the [MO] layers. This phenomenon is correlated to lines of diffuse scattering in reciprocal space observed for the different samples; it can be attributed to a second modulation wave occurring within the [MO] layers but with a lack of coherence along the stacking direction. Finally, the role of modulations as a driving force to relax strains in layered oxides and to allow non-stoichiometry is outlined.
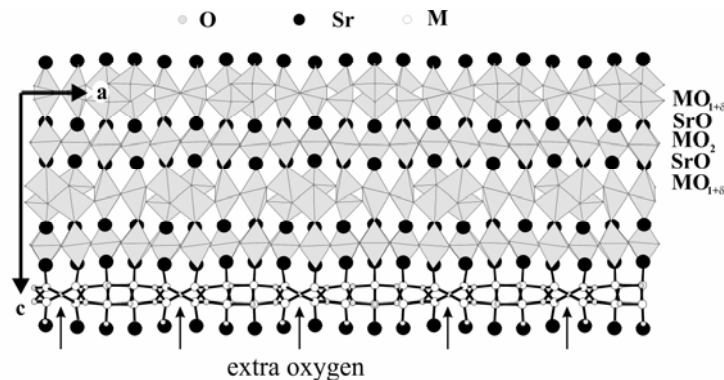

Figure 1: Projection of the structure along b.
M-O bonding scheme and polyhedra environment are represented.

[1] A. Yoshiasa, K. Ueno, F. Kanamaru and H. Horiuchi, Mat. Res. Bull., Vol. 21, 175-181 (1986).
[2] H. Leligny, S. Durčok, P. Labbé, M. Ledésert,. and B. Raveau. Acta Crystallogr. B48 407 (1992).
[3] W. Steurer and T. Haibach, International Tables for crystallography, vol. B (2nd edition), 486-518.

Symmetry of aperiodic crystals

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Dan Shechtman's discovery of quasicrystals, more than 2 decades ago, has fundamentally changed the way we think about such elementary concepts as crystallinity, long-range order, and symmetry [1-3]. Unfortunately, complicated mathematical descriptions in abstract high-dimensional spaces have stood in the way of disseminating our current understandings of these concepts to a broad community of scientists. How many physicists and chemists still teach their students that a crystal is a periodic repetition of a unit cell, even though the International Union of Crystallography has long ago abolished this definition of a 'crystal' [4]?

I shall review the notion of symmetry in crystals and explain—without the use of high dimensional tricks—exactly what we mean today when we say that a certain rotation is a symmetry element of a crystal. This redefinition of crystalline symmetry applies to all crystals known to date—from ordinary periodic crystals to incommensurately-modulated crystals, incommensurate composite crystals, and quasicrystals—and is used to generalize space-group theory to all of them [3,5]. When expressed in Fourier space this redefined notion of symmetry easily determines the pattern of symmetry-imposed extinction conditions in the diffraction pattern of a crystal.

If time permits I shall generalize the ordinary notion of crystalline symmetry to the notions of color [6] and magnetic [7-9] symmetry in crystals.

[1] R. Lifshitz: *The rebirth of crystallography*, Z. Kristallogr. **217**, 342-343 (2002).
[2] R. Lifshitz: *Quasicrystals: A matter of definition,* Foundations of Physics **33**, 1703-1711 (2003).
[3] R. Lifshitz: *The symmetry of quasiperiodic crystals,* Physica A **232**, 633-647 (1996).
[4] International Union of Crystallography—Commission on Aperiodic Crystals, Acta Crystallogr. A **48**, 922 (1992).
[5] N. D. Mermin: *The space groups of icosahedral quasicrystals and cubic, orthorhombic, monoclinic, and triclinic crystals*, Rev. Mod. Phys. **64**, 3-49, (1992).
[6] R. Lifshitz: *Theory of color symmetry for periodic and quasiperiodic crystals,* Rev. Mod. Phys. **69**, 1181-1218 (1997).
[7] R. Lifshitz: *Symmetry of magnetically ordered quasicrystals,* Phys. Rev. Lett. **80**, 2717-2720 (1998).
[8] R. Lifshitz and S. Even-Dar Mandel: *Magnetically ordered quasicrystals: Enumeration of spin groups and calculation of magnetic selection rules,* Acta Crystallogr. A **60**, 167-178 (2004).
[9] R. Lifshitz: *Magnetic point groups and space groups,* in *Encyclopedia of Condensed Matter Physics* (Elsevier, 2005). In press.