



International
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Commission on
Mathematical
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Crystallography



Commission on
Inorganic and
Mineral Structures



European
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SPECIAL INTEREST GROUP
Special Interest
Group No. 5
"Mineralogical
Crystallography"



XXIII European Crystallographic Meeting (ECM-23)

Satellite Conference on Mathematical and Theoretical Crystallography

Organized by the

Commission on Mathematical and Theoretical Crystallography of the International Union of Crystallography (IUCr-MaThCryst)

In cooperation with the

Commission on Inorganic and Mineral Structures of the International Union of Crystallography (IUCr-CIMS)

and with the

Special Interest Group No. 5 "Mineralogical Crystallography" of the European Crystallographic Association

4-6 August 2006 - Katholieke Universiteit Leuven

René Magritte room, ground floor of the Oude Valk ("Old Falcon") building, Tiensestraat 41



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PROGRAM

Friday, August 4

- 8:30 – 8:45 **Welcome address**
- 8:45 – 12:30 **Session 1: *Magnetic Subperiodic Groups and Magnetic Space Groups***
Daniel B. Litvin, Pennsylvania State University, USA
- 14:00 – 18:00 **Session 2: *Black-white symmetry, Ordered magnetics, Anisotropy of magnetic properties***
Hans Grimmer, Paul Scherrer Institute and University of Zurich, Switzerland

Saturday, August 5

- 8:30 – 12:30 **Session 3: *Graph theory: fundamentals and applications to crystallographic and crystallochemical problems. The vector method***
Jean Guillaume Eon, Universidade Federal do Rio de Janeiro, Brazil
- 14:00 – 18:00 **Session 4: *EPINET: Crystal nets from 2D hyperbolic geometry***
Stephen Hyde Australian National University

Sunday, August 6

- 8:30 – 12:30 **Session 5 *Modular categories and their principal features***
Emil Makovicky, University of Copenhagen, Denmark
- 14:00 – 17:30 **Session 6 *Symmetry constraints and modularity: tools to model inorganic crystal structures***
Giovanni Ferraris, University of Torino, Italy

30-minute coffee breaks at about 10:15 and 15:45

L1 - Magnetic Subperiodic Groups and Magnetic Space Groups

Daniel B. Litvin (*The Department of Physics, The Eberly College of Science, The Pennsylvania State University, Penn State Berks, P.O. Box 7009, Reading, PA 19610-6009, U.S.A., u3c@psu.edu*)

Magnetic Space Groups are defined and contrasted with mathematically related but distinct groups, as e.g. Heesch Groups, Dichromatic Groups, and Antisymmetry Groups. A brief history is given of the groups introduced that eventually led to magnetic space groups. There are two commonly used sets of notations for magnetic groups, the Belov, Neronova, & Smirnova (BNS) notation [1] and Opechowski-Guccione (OG) notation [2]. The differences between these two sets of notations are explained in detail. The interpretation of OG symbols is discussed and misinterpretations of the symbols are explained.

Published tabulations of the properties of magnetic space groups are reviewed. Unpublished International-like tables [3] for magnetic space groups are presented which include for each magnetic space group type: Diagrams of Symmetry elements and General Positions, Origin, Asymmetric Unit, Symmetry Operations, General and Special Positions and Symmetry of Special Projections. (A CD containing these and other tables will be given to the workshop participants). These tables define each of the magnetic space group types in five different formats: General Position Diagram, Symmetry Diagram, IT notation, Seitz Notation, and General Positions. How to convert the information among the various formats is discussed and workshop participants will have the opportunity of familiarizing themselves with these formats during problem solving sessions. Visualization of magnetic space groups is discussed and unpublished three-dimensional interactive general position diagrams are shown.

Subperiodic groups [4] are defined and the International-like tables for magnetic subperiodic groups [5] are introduced. The content and format of the tables of properties of magnetic subperiodic groups are the same as the analogous tables for magnetic space groups. Scanning of magnetic space groups is the process of determining the magnetic layer group symmetry of planes that pass through magnetic crystals. We shall show how magnetic space groups and this process of scanning can be used to determine the symmetry of domain walls in non-magnetic ferroic material.

- [1] Belov, N.V., Neronova, N.N., & Smirnova, T.S. (1955), *Trudy Inst. Krist. Akad. SSSR* **11**, 33-67. English translation in *Colored Symmetry* (1964), edited by W.T. Holser (Macmillan, New York.)
- [2] Opechowski, W. & Guccione, R. (1965), *Magnetic Symmetry*, in *Magnetism*, editors G.T. Rado and H. Suhl, Vol. 2A, Chapter 3 (Academic Press, New York).
- [3] Litvin, D.B., unpublished.
- [4] *International Tables for Crystallography, Volume E: Subperiodic Groups*, (2002) ,editors V. Kopsky & D.B. Litvin, (Kluwer Academic Publishers, Dordrecht)
- [5] Litvin, D.B., (2005), "Tables of Properties of Magnetic Subperiodic Groups," *Acta Crystallographica*, A61, 382-385 .

L2 - Black-white Symmetry; Ordered Magnetics; Anisotropy of Magnetic Properties

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First the definition of tensors and the application of the Neumann principle to property tensors are reviewed. The tensors describing the pyroelectric and the piezoelectric effect are discussed as examples. It is shown that the forms of these tensors can easily be derived for all crystallographic point groups and in all orientations in which they appear in the corresponding holohedry, once their form has been determined for the crystallographic point groups consisting only of rotations.

Then the behaviour of electric and magnetic dipoles is investigated with respect to the inversions of space, time and space-time. Including time inversion as a possible space group operation, one obtains 1651 Heesch-Shubnikov space groups instead of the 230 crystallographic ones, similarly 50 instead of 14 lattice types and 122 instead of 32 point groups. The 1651 space groups can be split into 230 monochrome, 230 grey and 1191 black-white ones. Black-white space groups have either a monochrome lattice and a black-white point group or a black-white lattice and a grey point group. It is shown how magnetically ordered crystals belonging to one of these two types differ in the magnetic effects that they admit.

The number of possible forms of a property tensor that changes sign under space inversion does not increase if we pass from the 32 crystallographic point groups to the 122 Heesch-Shubnikov point groups and from the two possible behaviours under space inversion to the four possible behaviours under space, time and space-time inversion. This is illustrated by considering the pyromagnetic, piezomagnetic and magnetoelectric effects. Examples of magnetically ordered crystals showing these effects are discussed. A synoptic table is presented, showing the Heesch-Shubnikov point groups admitting ferromagnetism, ferroelectricity, magnetoelectric effects of first and second order, piezoelectricity and piezomagnetism.

The following results are generally valid:

The restrictions imposed by the Heesch-Shubnikov point group of the crystal on the form of a property tensor depend only on its rank, internal symmetry and behaviour under inversions.

The description of this dependence can be split into two parts:

- 1) A scheme depending only on the point group of the crystal and the behaviour of the tensor under inversions.
- 2) A table giving the possible tensor forms, which depend only on the rank and internal symmetry of the tensor.

L3 - Graph theory: fundamentals and applications to crystallographic and crystallochemical problems – The vector method.

- **Fundamentals of graph theory**
- **Crystallographic nets and their quotient graphs**
- **Space group and isomorphism class**
- **Topological and geometric properties**

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The objective of the lecture is to present the graph-theoretic machinery which has been developed for analyzing topological problems in crystal chemistry. The key concept is that of crystallographic net, defined as a 3-connected graph whose automorphism group is isomorphic to some n -dimensional space group. Crystallographic nets, however, are more conveniently described, or derived, from their labeled quotient graphs. Although both objects are rigorously equivalent, the relationships between properties of the infinite net and the structure of its finite quotient are not straightforward. Chosen examples are examined to illustrate how symmetry as well as topological invariants of nets are encoded in the structure of their labeled quotients graphs.

The symmetry group of the net can be determined from the subgroup of the automorphism group of its quotient graph that respect the kernel of the cycle space, *i.e.* for which cycles or cycle combinations with null vector label are mapped on themselves. The symmetry of 3-dimensional realizations of the net (embeddings) is generally lower than that of the net. This leads to assigning their ideal symmetry to crystalline structures. Special emphasis is given to those automorphisms of the quotient graph that exchange its cycles (or loops) with different cycles (loops) having the same vector label; in this case the quotient appears to be partial. Such a situation arises from, or enables the description of symmetry loss due to periodic distortions of the embedding that do not affect topological properties of the framework, associated to *klassenleiche* group-subgroup relations. Some embedding questions are also considered. A general method for obtaining barycentric embeddings (aristotypes) is described.

Graphic and numerical invariants are then reviewed together with their relationships to the quotient graph. Simple illustrations are given using 2-dimensional nets. Among known graphic invariants are rings and strong rings; new invariants characteristic of infinite graphs are introduced. A *line* is defined as an acyclic, regular, connected subgraph of degree 2. A *geodesic line* is a line such that the unique path between two of its vertices is a geodesic path in the net. Lines and geodesic lines are the natural extensions of cycles and rings in periodic graphs. Strong geodesic lines and geodesic fibers are also defined. The latter invariants project on cyclic motifs of the quotient graph that are analyzed in detail. In particular, topological density, a numerical invariant of the net can be obtained directly from the cycle structure of the quotient graph that reflects the geodesic fibers of the net.

L4 - EPINET: Crystal nets from 2D hyperbolic geometry

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Crystalline 3D networks can be viewed as embeddings of 2D hyperbolic nets, where the embedding is done via a covering map involving 3-periodic minimal surfaces. Hyperbolic nets are enumerated using Delaney-Dress tiling theory, that relies on 2D hyperbolic crystallography. We use the concept of orbifolds to unify all the 2D geometries; mapping the usual point and plane groups onto elliptic and euclidean orbifolds respectively.

The essential tools for orbifolds and tilings are introduced via the concept of 2D manifolds. The results allow a topological picture of 2D symmetries, with discrete topological modules for translations, glides and reflections. A natural classification of 2D symmetries follows, with eight families based on the topological class of the orbifolds. The resulting patterns are collected in an online database, accessible at <http://epinet.anu.edu.au>.

L5 - Modular aspects of inorganic and mineral structures

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The polyhedral description of a crystal structure reveals a number of important features and also accounts for a substantial portion of its internal energy. However, with the increasing complexity of inorganic and mineral structures being determined, the importance of larger units, *moduli*, composed of a number of coordination polyhedra, becomes obvious both for the understanding and classification of these structures and for their thermodynamic stability.

The moduli are usually 0D, 1D or 2D fragments of simpler structure types, so called *archetypes*, which have been cut along certain crystallographic directions and recombined into a new structure according to a set of structural principles absent in the fragment interior. This process is often connected with changes in chemical composition. Structure-building principles that are active in the recombination process are, e.g., unit cell (chemical) twinning of different kind, crystallographic shear, non-commensurate interfaces, and coherent intergrowths.

Groups of structures built on the same principles, but with an incrementally increasing fragment size, have been named *accretional homologous series* or were alternatively defined as *polysomatic series*. The homologous approach allows further distinction, the so-called extensive and combinatorial categories. An entirely different, interesting group are *variable-fit structures* with two (sub)lattices present in one structure. Combination of the accretional and variable-fit principle leads to a new plethora of complex structures, including 'sliding series' and 'box-work structures'. An interesting problem is the extension of the homology principle to include a so-called *configurational homology*, beyond the limit of the usual 'isoelemental' concept.

Nature often breaks the straightjacket of pure, exact homology by introducing small but substantial changes into distinct structures of an otherwise clearly homogeneous structural family. Such structures can be denoted as *plesiotypes*. A special type of this category is a set of structures in which one set of layers/slabs is identical (or homologous) for the entire family whereas the other, alternating set differs profoundly from a member to a member. These structures have been denoted as *merotypes*.

Plesiotype and merotype families can be defined at different levels of generality, helping to construct a hierarchical, rather than one-level classification of structures.

Polytypes are a special type of modular structures; in some cases of practical usage, especially on a configurational level, they can also be described using one of the previous concepts. The OD-theory of polytypy has been worked out to a considerable detail and, perhaps, the time has arrived to systematize the crystal-chemical/structural aspects of this phenomenon, touching the subtle questions of the concept of polytypy. Besides 'proper' (*OD-* and *non-OD polytypes*), with structurally unmodified layers, '*improper*' polytypes can be recognized, with individual modifications of component layers, as well as *pseudopolytypes* between which pronounced changes in bonding patterns occur, and *endopolytypes* in which only (e.g.) the cation component is subject to polytypy whereas the anionic framework remains (in principle) unchanged. Furthermore, *non-commensurability* and *semicomensurability* can play a role in the generation of polytypes. Undoubtedly, further such variants of polytypes will be recognized.

All these categories have been painstakingly developed by a number of scientists, whose contributions will be duly mentioned at the appropriate points of the lecture, together with the most instructive structural examples from the inorganic and mineral realm for the concepts mentioned. For recent synopsis of the authors and concepts, see Ferraris et al. [1].

[1] Ferraris, G., Makovicky, E. and Merlino, S. (2004): Crystallography of Modular Materials. IUCr Monographs on Crystallography **15**, Oxford Sci. Publications.

L6 - Symmetry constraints and modularity: tools to model inorganic crystal structures

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It is well known that modelling a crystal structure is a task harder for non-molecular than for molecular structures: in fact, in the latter case the process can often be reduced to finding the packing of known molecules. The emphasis on coordination polyhedra in describing inorganic (i.e., non-molecular) structures is usual since long time; however, apart simple structures, modelling a structure just starting from coordination polyhedra is a hopeless task. In recent years, it has been recognized that some modules (fragments) consisting of several coordination polyhedra may be recurrent in different crystal structures. Classical examples are (i) polytypes, i.e. structures based on different stacking of a same basic layer, and (ii) layer silicates all based on tetrahedral (*T*) and octahedral (*O*) sheets grouped either as *TO* or *TOT* layers.

Several procedures useful to describe and model structures based on recurrent modules are reported in literature, as recently systematically discussed in a book dedicated to the crystallography of modular materials [1]. Among several approaches, the lecture will focus on the so called polysomatic series which are a subclass of the homologous series. All members of a polysomatic series share two or more modules that have definite chemical composition and lattice dimensions. Different modules (here supposed to be layers) must share common lattice dimensions in order to match at their common interface when are stacked along a direction. For sake of simplicity, let us refer to the most common case of two modules (say *A* and *B*); a periodic stacking of intercalated *mA* and *nB* modules forms a crystal structure with chemical composition A_mB_n , including the end-members *A* and *B*. The same symbol A_mB_n is used to represent the related series. The building principle of a polysomatic series implies that chemical composition and lattice dimensions of each member are linear functions of those of the single modules. Note that for a given composition A_mB_n , different sequences of the modules *A* and *B*, i.e. different polymorphs (in case, polytypes), are possible.

An introductory description of some classical polysomatic structures (e.g., biopyriboles and structures based on perovskite modules) and of basic structures which are well constrained by symmetry will help to focus the concepts.

Following the introductory part, examples of modelling crystal structures of inorganic compounds, which either belong to known polysomatic series or, at least, are similar to known crystal structures, will be illustrated. The main steps of the modelling process are as follows.

1. Determination of the chemical composition.
2. Determination of the lattice parameters and of the space group (or at least of the crystal system). These data usually can be obtained only from powder-diffraction patterns and/or transmission electron microscopy. In fact, if single crystals suitable for X-ray single-crystal methods are available, presumably (even if not necessarily) the crystal structure can be directly solved from diffraction data.
3. Search of known structures with which, according to the chemical composition and lattice dimensions, the unknown structure shares structural modules.
4. Building of a structure model which matches the known chemical and crystallographic data.
5. Assessment of the structure geometry (bonds and angles) via refinement procedures like Distance Least Squares (DLS, [2]).
6. Validation of the structure model via crystal-chemical tests and comparison between calculated and observed diffraction patterns.
7. Refinement of the structure model against diffraction data as far as the complexity of the structure and the quality of the experimental data allow it. Often, the best agreement between calculated and observed data can be assessed only by trial.

Some worked examples of inorganic structures modelled according to the scheme given above will be presented. Most of the examples concern the polysomatic and merotype series of heterophyllosilicates. A polysomatic series is said to be merotype if only a part (e.g. one) of the building modules are shared by all members of the series, being other modules specific of each member. Heterophyllosilicates are a large family of layer titanosilicates based on *HOH* layers which can be formally derived from the well known *TOT* layers of the phyllosilicates (layer silicates) by substituting rows of disilicate tetrahedra by rows of five- or six-coordinated Ti (and vicariant elements). Three main types of *HOH* layers are known: bafertisite-, astrophyllite- and nafertisite-type. Other examples are related to microporous rhodesite-like structures [3].

[1] Ferraris, G., Makovicky, E., Merlino, S. (2004). *Crystallography of Modular Materials*. IUCr/Oxford Univ. Press.

[2] Baerlocher, Ch., Hepp, A., Meier, W.M. (1978). *Manual DLS-76. A Program for the simulation of crystal structures by geometric refinement*. ETH, Zurich.

[3] Ferraris, G., Merlino, S. (Eds.) (2005). *Micro and mesoporous mineral phases*. Mineralogical Society of America.

P1 - The methods for topological analysis of 3-periodic nets

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Topological indices (Schläfli symbols, Vertex symbols, coordination sequences) commonly used in crystal chemistry to recognize topologies of crystal structures are discussed. The algorithms to calculate them are implemented in the program package TOPOS [1]. The efficiency of these procedures has been justified by analyzing more than 18,000 3-periodic nets. Although it is well known that none of the topological indices determines net topology up to isomorphism, a combined use of them allows to identify net topology unambiguously in many cases [2].

A pair of cubic sphere packings 4/3/c25 and 4/3/c26 derived by W. Fischer [3] is up to now a unique example of the two non-isomorphic 3-periodic nets having identical all the topological indices. To distinguish between topologies in this case, one should consider 'proper' super- and subnets of the nets to be tested. By 'proper' supernets (subnets) we mean graphs that result from initial ones after addition (omission) of some generators that play analogous roles in the initial graphs. For isomorphic nets all the sets of ('proper') super- and subnets are necessarily the same.

To illustrate this, let us consider the above mentioned pair of the cubic sphere packings. The sets of symmetry operations that give rise to the sphere contacts are $(y,z,x; z,x,y; 1/4-z, 1/4-y, 1/4-x; 1/4+z, 1/4-y, 3/4+x)$ for the 4/3/c25 packing and $(y,z,x; z,x,y; 1/4-z, 1/4-y, 1/4-x; 1/2-x, y, -z)$ for the 4/3/c26 packing, respectively. The additional generator can be chosen as the symmetry operation $1/4-y, 1/4-x, 1/4-z$. The sets $(y,z,x; z,x,y; 1/4-z, 1/4-y, 1/4-x; 1/4+z, 1/4-y, 3/4+x; 1/4-y, 1/4-x, 1/4-z)$ and $(y,z,x; z,x,y; 1/4-z, 1/4-y, 1/4-x; 1/2-x, y, -z; 1/4-y, 1/4-x, 1/4-z)$ generate the sphere packings 5/3/c30 and 5/3/c31, respectively, to be unambiguously differentiated by Vertex symbols. This fact proves the 4/3/c25 and 4/3/c26 sphere packings to be non-isomorphic. It is curious that these two packings are self-catenating but differ by modes of catenation.

To conclude, let us note that the combination of different topological descriptors and net relationships can be successfully used to determine net topologies.

[1] <http://www.topos.ssu.samara.ru>

[2] O'Keeffe, M., Hyde, B. G. (1996). Crystal Structures I: Patterns and Symmetry. Washington: Mineralogical Society of America.

[3] Fischer, W. (1974). Z. Kristallogr. 140, 50-74.

P2 - The 18-electron rule in the structure of some lanthanides complexes*Vologzhanina A.V. (Samara State University, Samara, Russia), vologzhanina@mail.ru*

One of the most important problems of modern crystal chemistry is the search for relationship between the chemical composition and the structure of a compound. The structures of all aqua-, hydroxo- and nitrate- complexes of lanthanides ($\text{Ln} = \text{La} - \text{Lu}$) were analysed by means of stereoatomic model of an atom. Within this model, atoms are approximated by soft, easily deformable spheres of constant volume, which form in the crystal structure the Voronoi-Dirichlet partition. The number of electrons (E_i) donated by a ligand (**Lig**) to a Ln atom is proportional to the solid angle (Ω_i) of the Voronoi-Dirichlet polyhedron face corresponding to the Ln – Lig bond. Assuming that f-electrons of Ln atoms do not take part in chemical bonding and 18 electron shell of the Ln atom are to be the most stable, it becomes possible to calculate E_i as $E_i = 0.18 \times \Omega_i$.

The primary crystal structures information was selected from structural databases of inorganic [1] and coordination [2] compounds. All the necessary calculations such as determination of atoms coordination numbers, the solid angles Ln – Lig calculation and their analysis have been done by means of the TOPOS program package [3]. In databases [1, 2] there exist 83 and 440 lanthanides compounds, containing at least one hydroxo- or nitrate-group, and 43 compounds, containing aqua-complexes $[\text{Ln}(\text{H}_2\text{O})_n]^{3+}$. It was found out that aqua in lanthanides compounds is always a monodentate terminal ligand, hydroxide anion is mostly a monodentate bridge ligand and nitrate anion usually is bidentate ligand. Results of E_i calculation for aqua, hydroxide anion and nitrate anion are presented in Table 1.

Ligand	E_i	The analysed number of ligands
OH ⁻	2.05(27)	184
H ₂ O	2.10(22)	937
NO ₃ ⁻	1.65(16)	1583

Table 1 The E_i meaning for some oxygen containing ligands

As it can be seen from Table 1, an oxygen atom of any ligand within a double error is a donor of 2 electrons that is all Ln-O bonds in compounds under discussion are ordinary. This fact also confirms our assuming of 18-electron shell stability for lanthanides.

Provided that for a lanthanides complex the E_i meanings of all ligands have been calculated, it becomes possible to find out the number of electrons in lanthanide shell (N_{Ln}) as

$$N_{\text{Ln}} = \sum_i E_i \cdot d_i \cdot$$

The analyses of complexes $[\text{LnLig}_n]^z$ ($\text{Ln} = \text{La} - \text{Lu}$, $\text{Lig} = \text{H}_2\text{O}$, OH^- and/or NO_3^-), both homo-, and heteroleptic, have shown that most of the Ln atoms in their structures have $N_{\text{Ln}} = 18 \pm 1.5$ electrons. Besides, whenever for the complexes $[\text{LnLig}_n]^z$ with the same number and nature of ligands increase in the lanthanide atomic number is accompanied by increase of N_{Ln} for more then 19.5 or decrease for less then 16.5 electrons, a structure change becomes possible. It may be a change in a type of ligand coordination or remove of a ligand from a complex. It was established that this method allows one to evaluate a stability of a complex, to predict the structure of a complex and coordination number of a lanthanide atom.

This work was financially supported by Ministry of education and science of the Samara region (grant 202E2.5 K).

- [1] Inorganic crystal structure database. FIZ Karlsruhe & NIST Gaithersburg, 2004.
 [2] Cambridge structural database system. November 2004 Release.
 [3] Blatov V.A., Shevchenko A.P., Serezhkin V.N. (2000) *J. Appl. Cryst.* **33**: 1193.

P3 - The intensity of the strongest reflection in a thin resolution shell

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We apply Gumbel-Fisher-Tippett (GFT) extreme value analysis to evaluate the distribution, expectation value and standard deviation of the intensity J of the *strongest* reflection in a given resolution shell in the X-ray diffraction pattern of a crystal with many scattering atoms in the unit cell. For convenience, we measure intensities in units of the *average* reflection intensity in the resolution shell, and for simplicity, we treat centric and acentric reflections separately. For acentric reflections, the expectation value μ and standard deviation σ of J are $\mu = \ln n + \gamma$ and $\sigma = \pi/\sqrt{6}$, where n is the number of crystallographically independent reflections in the resolution shell and $\gamma \approx 0.577$ is the Euler-Mascheroni constant. For centric reflections with expectation value 1 for the intensity, the corresponding expressions are $\mu = 2(\ln n + \gamma) - \ln(\pi \ln n)$ and $\sigma = 2\pi/\sqrt{6} - \pi/(\sqrt{6} \ln n)$. Extensive numerical simulations show that our formulas are excellent approximations for random atom configurations at all resolutions, and good approximations for real protein crystal structures in the resolution range between 2.5 Å and 1.0 Å (Fig. 1 and not shown).

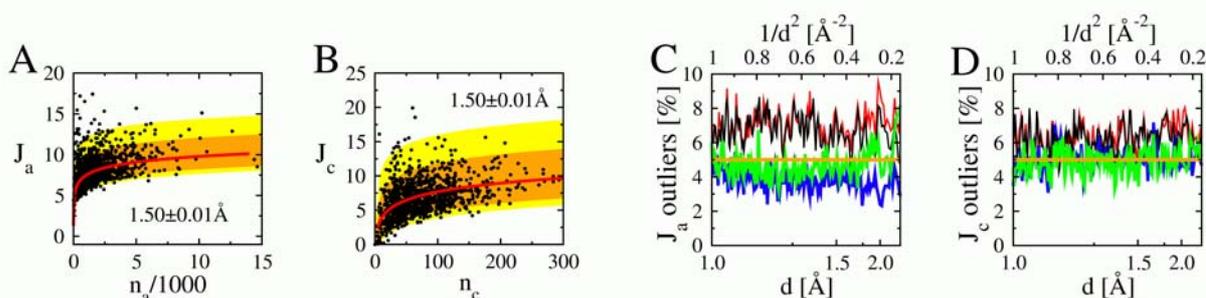


Figure 1: Intensity of the strongest acentric (A,C) or centric (B,D) reflection in a thin resolution shell for real structures from the Protein Data Bank (PDB, release date April 18th, 2006) as a function of the number of reflections in the shell. (A,B) Intensity of the strongest reflection in the shell $1.5 \text{ \AA} \pm 0.01 \text{ \AA}$. The red line indicates the expectation value for random atom arrangements and the orange and yellow areas mark the predicted 90% and 99% confidence intervals for random atom arrangements. (C,D) Percentage of outliers above (black and red) and below (blue and green) the 90% confidence interval for real structures from the PDB as a function of resolution. Overlapping resolution shells were used in the analysis. The width of each resolution shell was chosen so that its reciprocal space volume matched the volume of the $1.5 \text{ \AA} \pm 0.01 \text{ \AA}$ shell. Blue and red lines are based on the normalization with respect to actual shell intensity averages, and green and black lines are based on intensities calculated from normalized structure factors, which in turn are based on smoothed intensity averages. For random atom arrangements with many scatterers, the black, red, blue and green lines should all converge at the indicated 5% level (orange line).

P4 - An alternative approach for the description of modulated structures using differential geometry

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Differential geometry is a theory that has been existing for one and a half century and is much solicited in many physical topics, but not a lot in crystallography. In fact, Hans Wondratschek [1] hints at this mathematical topic, when introducing two spaces for the description of the symmetry operations : the *point space* and the associated *vector space*. In our work, we think of \mathbf{R}^n as a differential manifold in which we consider n -dimensional lattices, be they smoothly modulated or not. The focus of our viewpoint is to say that each node of the lattice is linked to an origin point not by a vector, but by a curve belonging to a family $\{c_\lambda \mid \lambda \in M\}$, where M is a \mathbf{Z} -module. If we parametrize each of these curves between 0 and 1, we can see that the extremities of the corresponding velocity vectors at 0 generate a periodic lattice of translations in the tangent space. Using this approach, it seems that the symmetry of modulated structures can be described without erring in a higher dimensional space (superspace) and the diffraction pattern of such structures could be better understood considering the Fourier transform in the tangent space.

- [1] H. Wondratschek, *Introduction to space-group symmetry: Basic concepts*, taken from: *International Tables for Crystallography*, Vol. A, pp 720 – 721, Kluwer Academic Publishers, Dordrecht, 2002.

P5 - Problems and nature ideas of their solution

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The Universe according to A.A. Bogdanov consists of different systems (sets). Every system consists of elements. Elements are the alphabet of any system. All the members of any system are made up of combinations of elements. The main problem of nature is to combine elements to form stable members of sets.

Nature gives us facts: The alphabet of elements and members of systems. Our problem is to classify known members in such a way as to have the ability to predict new ones. To predict new members one has to know the ideas of nature by their combinations. The theory of order to order transformation (OO) arose simultaneously with the inception of the distinguishing of crystalline structures (i.e. different superstructures and polytypes). Belov's Order Theory (O-Theory), published in 1947, dealt with structural units of equal sorts (closely packed layers), their own symmetry and symmetrical variants of conjugation. A correlation of letter formulas (h, k, hk...), Zhdanov's formulas and space groups were established. The Belov subclass with the greatest common divisor (GCD) $p3m1$ containing eight space groups was established for close packings. O-Theory was extended to OD-Theory (Dornberger-Shiff et al., 1964...) to DO-Theory (Smirnova et al. 1952...) to Rr-Theory (Deloneu). The local principle of identity and unindifference was used as universal in extended O- and DO- Theory. Two principles allow the whole structure to be built from one local point. For all GCD of 0 – 3 dimensional symmetry groups Belov classes were established. Many Belov subclasses were set up for many different series, both realized and possible (Kripyakevich et al, Smirnova et al, Arakcheeva et al.). Kepler - Shubnikov nets were used to represent the structure types. A method of coordinate spectra was worked out. A modular aspect for all structure types was proposed. Some basic 0 – 3 dimensional modules were established. This approach and the extended OD-theory are close to each other. There is similarity and difference between ideas of nature and mathematics. Both of them work with elements. In mathematics there may be an infinite number of elements and their combinations. In nature that is impossible. On the first step of organization a system has a few different simple elements and their combinations. Some combinations of elements of previous level later become new elements for next level. Systems change in terms of quality, but quantitative ratios are conserved from system to system. Quantitative ratios obey the law of whole small numbers. This is easy to see on the linear and planar complication schemes (LCS and PCS) of Weiss-Brococci-V. Goldschmidt-Farey-Smirnova. Lattice parameter ratios with pronounced frequencies are composed of numbers and operations upon them (Gelder, Janner). Here is the LCS from combinations of numbers (basic ratios are bold, latent ratios – in quotas): "11", 22, 33, 332, **56**, **34**, 342, 343, **7.10**, **23**, 231, "35", 352, **12**, 24, 36, **25**, **38**, 382, 383, **13**, 26, **3.10**, **27**, **15**, **16**, **1.10**, **2.15**, 1, 2, 3, 5, 6, 7, 9, .10, .14, .15. Ratios m/k (Fischer) for tetragonal sphere packings with minimal density are presented here as LCS "11", 33, 44, 55, **45** and 54, **34** and 43, "23", 46 and 64, **35**, **47**, "12", 36, 48, **37**, **38** and 83, "13", 39, **3.10** and .10.3, **2.11**, "14", 3.12 and as PCS of basic ratios.

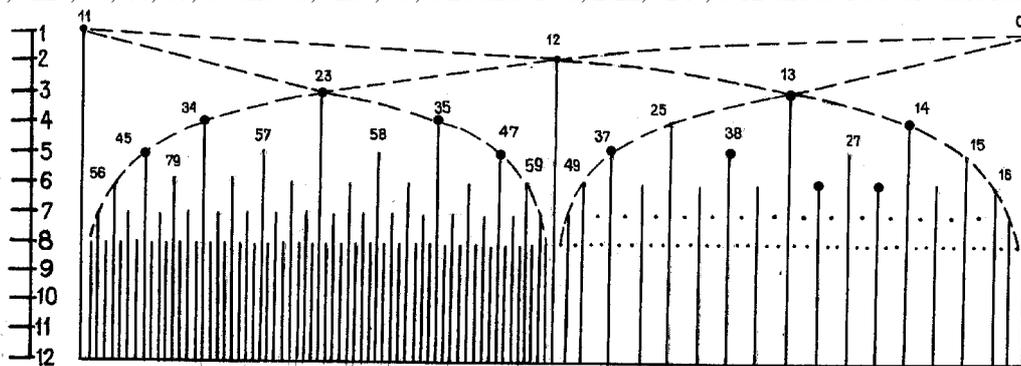


Figure 1 Planar Complication Scheme of Weiss-Brococci-V. Goldschmidt-Farey-Smirnova, Belov ratios m/k in Tetragonal Sphere Packings with Minimal Densities and Subunities

The main idea of nature is to allow everything that can be but to survive is up to everyone. It's up to us to understand what can be, to predict it.