

MS15-P12 **Number-theoretic Approaches to the Description of Crystal Structures.** Wolfgang Hornfeck, *Institut für Materialphysik im Weltraum, Deutsches Zentrum für Luft- und Raumfahrt (DLR), 51170 Köln, Germany*
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Crystallographic group theory is commonly regarded as the method of choice for the description of crystal structures and related phenomena such as phase transformations, antiphase domain formation and twinning.[1] Symmetry alone, however, merely comprises a *qualitative* picture.

On the contrary, number theory seems to be far less explored within a crystallographic context, whereas it possibly allows for a more *quantitative* arithmetic approach.

An illustrative example is given by so-called *multiplicative congruential generators* (MCGs), i.e. recurrence relations of the form $Z_{n+1} = mZ_n \pmod{M}$, first introduced by Lehmer for the generation of *pseudorandom* number sequences.[2] However, Marsaglia later noted that MCGs exhibit an intrinsic sublattice structure,[3] which was shown to have some implications for the description of crystal structures.[4,5]

Another example is due to the *bit-reversal, quasirandom* number sequences of van der Corput,[6] which exhibit features related to quasiperiodic binary substitution tilings.

Both approaches share a common basis, as the integer sequences involved for the generation of the corresponding two- or three-dimensional point sets and their coordinate description are mere *permutations* of a finite set of successive natural numbers.

Notably both methods have their primary application in the generation of *random* numbers, which sheds some light on the subtle interrelations between distinct states of order.

Following the aforementioned number-theoretic construction principles allows for the systematic (algorithmic) generation of artificial crystal structures (*permutation structures*), as well as their combinatorial enumeration and classification.

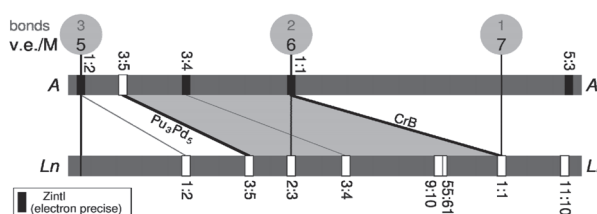
The peculiar structure of β -Mn has already identified as a near-miss to these envisioned permutation structures.

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MS15-P13 **A systematic crystal chemical study of mixed stann-ides/germanides.** Michael Jehle^a, Ines Dürr^a, Saskia Fink^a, Britta Lang^a, Caroline Röhr^a, ^a*Institut für Anorganische und Analytische Chemie, University of Freiburg, Germany*
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Starting from the extremely rich but quite diverse structural chemistry of binary lanthanum tetrelides, ternary mixed La stann-ides/germanides have been synthesized which not only present substitutional variants of the binary border phases, but also themselves form new singular structure types [1,2]. This work was now extended to the heavier rare earth elements (*Ln*) Gd (smaller ionic radius) and Yb (flexible valency), and the alkaline earth elements Ca, Sr and Ba (*A*), which form mostly electron precise Zintl phases (black symbols). In the crystal structures of the binary *A* compounds, a partial statistical (e.g. BaGe_{0.45}Sn_{1.55}, substituted BaSn₂ [3]) as well as an ordered (e.g. SrSnGe, KSnAs type) distribution of Ge and Sn (*M*) has been observed.



Despite their different valence electron numbers, the binary (and the presented ternary Ge/Sn) 1:1 and 3:5 tetrelides of *Ln* and *A* are isostructural forming common structure types (CrB and Pu₃Pd₅ resp.), which are known to be electronically flexible [4,5]. Because of their isolated and chemically different tetrelide anions, the electron-rich phases $Ln_{11}M_{10}$ (Ho₁₁Ge₁₀ type) exhibit a wide variety of Sn/Ge substitution (e.g. Yb₁₁Sn_{4.2}Ge_{5.8}), which allows a detailed study of the tetrel distribution ('coloring') in the anions. Inbetween the *Ln:M* composition 1:1 and 3:5 ternary mixed stann-/german-ides exhibit a wide variety of different compositions and structures not known from any binary border phase. These mixed tetrelides of compositions 55:61 (La₅₅Sn_{36.6}Ge_{24.4} [1]), 9:10 (La₉Sn_{6.7}Ge_{3.3} [2] and Gd₉Sn_{6.1}Ge_{3.9}), 3:4 ((La/Gd)₃Sn_{0.9}Ge_{3.1}, Er₃Ge₄ type), 2:3 (Yb₂SnGe₂, Mo₂FeB₂ type) and 3:5 (La₃Sn_{4.4}Ge_{0.6} [2], La₃In₄Ge type) exhibit only small deviations from the Zintl electron count. Their complex structures show different *M* anions/bonding modes e.g. the trigonal planar Ge coordination, which is only possible due to the *s-p* band mixing of the lighter Ge and the square-planar surrounding of hypervalent Sn. This differentiation of the bonding mode, together with the contribution of partially occupied *Ln-d* states, decreases or even prevents a Ge/Sn phase width and in turn creates the rich structure chemistry of mixed *Ln* tetrelides in this composition range.

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