MS39 O3

Superspace Finder: Behind the Interface Ivan Orlov, Lukas Palatinus and Gervais Chapuis, *Ecole Polytechnique Fédérale de Lausanne, CH-1015, Switzerland.* E-mail: Ivan.Orlov@epfl.ch

Keywords: superspace symmetry, aperiodic structures, crystallography in higher dimensons

Apperiodic structures do not exhibit three-dimensionnal translation symmetry. However, in, higker-dimensional translation space symmetry can be restored in the so-called superspace. Commensurately modulated structures and therfore, their symmetry may be described in two ways: by the (3+1)D superspace groups, when they are considered as usual 3D periodic superstructures. Such dualism suggests, that we are capable to find relations between (3+1)D superspace groups and the 3D ones and vice versa. The Superspace Finder is a Web-application, providing such transformations and conditions for corresponding commensurate cuts. A dedicated database stores a complete set of data for (3+1) to 3D group relations obtained for the first time. Along with its fundamental value this net provides vats ground for investigations both in theoretical and practical fields, for ewample, allowed space group sequences for phase transitions. Another question is for example what can we learn from a statistical study of all possible (3+1) to 3D relations?

[1] http://superspace.epfl.ch/finder

MS39 O4

Stuffing patterns in CoSn-frameworks: a space model based on low-energy antiphase boundaries. Daniel C. Fredrickson[a], Sven Lidin[a], Gerard Venturini [b], Jeppe Christensen[a], [a]*Inorganic Chemistry, Stockholm University, Sweden.* [b]*Laboratoire de Chimie du Solide Mineral, Universite Henri Poincare-Nancy I, France.* E-mail: danny@inorg.su.se

Keywords: Superspace symmetry, Rietveld structural refinement, electronic structure calculations

The CoSn-type phases contain large interstitial void spaces, which frequently allow the incorporation electropositive guest atoms, such as rare earth elements. In this stuffing process, an intriguing ordering occurs between the neighboring void spaces leading to a family of long-range superstructures. In the YFe_6Sn_6 and $TbFe_6Ge_3Ga_3$ phases, for example, the unit cells contain 16 and 34 CoSn subcells, respectively. Recently, these long-period superstuctures were found to give way to incommensurability in the $ScFe_6Ge_{6-x}Ga_x$ system [1]. In this work, we derive a superspace model for the structural features observed in this series of structures, incorporating both the commensurate and incommensurate examples. In the resulting model, the family is generated from a 3+1D unit cell in the orthorhombic superspace group Xmmm(0β0)000 or its monoclinic subgroup X2/m(αβ0)00, in which X represents a 4D centering with three vectors: (½,½,0,0), (0,0,½,½), and (½,½,½,½). The central feature in this description is the use of a crenel modulation function to produce distributions of occupied and vacant interstitial spaces. The utility of this superspace model for structure solution is demonstrated with the crystal structure refinements of four $ErFe_6Ge_{6-x}Ga_x$ phases, two commensurate and two incommensurate, from powder X-ray diffraction data. The results confirm a trend observed in the corresponding Sc series [1]: a gradual increase in the length of the q-vector as Ge is progressively replaced with Ga. To investigate the possibility of electron-count control in this progression, we performed electronic structure calculations, at the LDA-DFT level, on several commensurate members of this family. These calculations indicate that the changes in valence electron count upon substituting Ga for Ge is accommodated facilely by a dense set of non-bonding Fe *d* levels, and that magnetic ordering plays a significant role in stabilizing these phases. As these aspects of the electronic structure are virtually independent of the composition and stuffing pattern adopted, the structural preferences in this series appear to be driven by other differences between Ga and Ge, for instance in size or electronegativity.

[1] Venturini, G. *J. Alloys Comp.* 2001, *322,* 190-197.

MS39 O5

Disorder Deciphering from Super Space Formalism, Olivier Pérez, Nicolas Barrier, Jean Michel Rueff, Laure Adam, Anne Guesdon and Dominique Grebille, *CRISMAT/Ensicaen/CNRS, Caen, France.*
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Keywords: diffuse X-ray scattering, disordered structure, aperiodicity

Single crystal X-ray diffraction always occupied a central position for the structural investigations of new materials. These last years, the systematic use of 2d detectors led to the increasingly frequent observation of complex diffraction phenomena such as aperiodicity or diffuse scattering. The development of the super space formalism [1] allowed an accurate determination of the aperiodic structures. The understanding of disorders associated with the diffuse scattering is more questionable. Classical approach considers only the long range order coherent part of the diffraction pattern and leads to an average structure of the material. Thereafter, the disorder must be elucidated thanks to the vivid imagination of the crystallographer. But diffuse scattering phenomena are related to short range order. The real structure of the material is then somewhere in between the average structure and an ideal perfectly ordered structure. Then, the description of this ideal ordered structure gives an insight of the local order of the real structure. For example, the $CaTeO_4$, $NH_4Fe_2(PO_4)_2$ and $P_4W_{18}O_{62}$ phases show a diffraction pattern where both punctual reflections and diffuse lines coexist. Classical crystallographic studies lead to atoms split over two too close positions for $CaTeO_4$ and $NH_4Fe_2(PO_4)_2$ while an elongation of the atomic displacement parameter is observed for $P_4W_{18}O_{62}$. For the two first compounds the disorder prevents the determination of the local atomic environments whereas it hides the atomic displacements driving the charge density wave observed in the third one. In all these examples the ideal ordered structure has been researched. In this purpose and following symmetry considerations, an ideal diffraction pattern is designed by replacing the diffuse scattering, observed in the real reciprocal space, by punctual reflections. A partial integration of the diffuse lines from the experimental frames allows us to assign intensities to these additional reflections. A reduced number of extra reflections is thus generated. Super space

formalism is then very useful for a modeling of this pseudo long range order; it allows the building of a model step by step and improves the convergence by reducing the number of refinement parameters. The structure of the perfectly ordered material leads to a peculiar NH_4^+/Fe order for $NH_4Fe_2(PO_4)_2$ [2], a tilting of the TeO_5 pyramid for $CaTeO_4$ and a displacement of W inside WO_6 octahedra for $P_4W_{18}O_{62}$. A with comparison the average structure provides an accurate description of the real local structure.

[1] De Wolff P.M., Janssen T. and Janner A., Acta crystallogr. A37, 625 (1981).
[2] Pérez O., Adam L., Guesdon A., Daturi M. and Raveau B., Acta crystallogr. B (submitted)