MS035.O01

Applications of the superspace concept in crystal chemistry

Gervais Chapuis[1]
[1]*EPFL Lausanne, Lausanne, Switzerland*
E-mail: gervais.chapuis@epfl.ch

The concept of superspace was introduced with the aim to extend the application of crystallographic symmetry to incommensurately modulated (IM) and composite (COMP) structures, both belonging to the class of aperiodic structures. Superspace symmetry is now universally accepted and routinely applied to describe them.

Superspace can however do much more. First, its application is not only limited to the description of aperiodic structures in (3+n)-dimensions where n varies between 1 and 3. It can also be applied to the description of superstructures and it can lead also to the description of conventional structures. In other words, the concept of superspace can be used to describe families of compounds where both aperiodic and periodic cases occur. Moreover, it appears frequently that the superspace description of one of its aperiodic member allows to derive the possible three dimensional symmetries of the periodic members of the same family of compounds. Examples are scheelites [1], calaverite, hexagonal ferrites, palmierite and PbO_2. In particular, it is possible to derive and/or predict polytypic modifications as in the temperature dependent phases of $K_5Yb(MoO_4)_4$ [2] and pharmaceutical Cimetidine, $C_{10}H_{16}N_6S$.

Another interesting aspect of crystal chemistry concerns characteristic interatomic distances. IM structures can essentially simplify the statistical estimation of this property, which is traditionally based on analysis of many different compounds. For instance, it was found that the estimation of K-O, In-O and P-O distances based on about 3000 3D compounds is equal to the statistical distribution in a single $K_3In(PO_4)_2$ IM structure [3]. All coordination numbers (CN = 6, 8, 10, 12) found for K in about 1500 3D structures occur in this single IM structure.

The example of Eu-containing molybdates with variable compositions and (3+n)D IM structures is an interesting illustration of the superspace approach to explain physical properties like $e.g.$ luminescence. It was shown that the luminescent efficiency is correlated to specific associations of Eu atoms in the cationic substructure, which are aperiodically ordered.

The superspace approach is particularly efficient for the investigation of high-pressure structures of chemical elements where a majority of them exhibits aperiodic structures above normal pressures. Our recent study of BaIV IM phase reveals an interesting case of atomic density waves in the range of 16.6 - 19.5 GPa.

Our presentation will illustrate a few examples of the use of superspace to discover new relations between crystal structures and possible applications in crystal chemistry.

[1] Arakcheeva, A. & Chapuis, G. (2008). Acta Cryst. B64 12-25.

[2] Arakcheeva, A. & Chapuis, G. (2006). Acta Cryst. B62 52-59.

[3] Arakcheeva, A. et al. (2003). Acta Cryst. B59 17-27.
Keywords: structure relations properties, superspace, aperiodic structures