The application of the superspace approach in mineralogy.

Alla Arakcheeva[*], Gervais Chapuis[**], Nicolas Meisser[*] & Philippe Thélin[*]

*Institut de Minéralogie et Géochimie & Musée cantonal de géologie, Université de Lausanne, CH-1015 Lausanne, Switzerland; e-mail: allaarakcheeva@gmail.com
**Laboratoire de Cristallographie, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

Crystallography of aperiodic systems is a relatively new field in structural sciences and probably one of the most active branch in crystallography both from the theoretical and experimental points of view. Aperiodic crystals are perfectly ordered materials with long range order but lacking the three dimensional periodicity as observed in classical crystals. However, in order to recover periodicity, these structures can be described in a higher dimensional space, the (3+d)-superspace. This approach is currently applied with success for the determination and description of incommensurately modulated crystal structures (IMS). The superspace approach opens also a new scope for the characterisation of chemical bonds, for the study of phase transitions, for the classification, description and prediction of structure families and their stabilisation conditions. Natural minerals are best-suited materials for the application of the superspace formalism, because some aspects concerning their genesis and related geological aspects can be clarified at the same time.

One can claim that the development of crystallography was traditionally initiated by mineralogy. The objects, which primarily instigated the mathematical description of crystal forms and then crystal structure determinations, were minerals. Crystal chemistry, which evolved in the second half of the 20th century, is essentially based on the large amount of structure determinations of natural minerals. In material science, mineral names are used for the notation of structure types. It is not surprising that precisely the mineral natrite, Na_2CO_3, has played a fundamental role in the development of the superspace theory. The structures of anhydrous sodium carbonate appear to be remarkable milestones in the development of the superspace approach during the last 50 years. In 1964, P.M. de Wolff used natrite in order to describe structures exhibiting satellite reflections (Brouns et al. 1964). Ten years later, the incommensurately modulated structure was the first to be refined in (3+1)-dimensional superspace (van Aalst et al. 1976; de Wolff 1974). However, an improved refinement of this structure appeared three decades later, in 2003, from a synthetic analogue of this mineral (Dusek et al. 2003). The (3+1)-dimensional description of the diffraction pattern and incommensurately modulated structure determination did reveal the role played by the second coordination sphere in the interatomic interactions which are at the origin of the phase transitions in Na_2CO_3. It should be mentioned, that the incommensurately modulated crystal structure of the mineral natrite has just been refined recently by us (Arakcheeva & Chapuis 2005).

We propose to apply further the recent developments on the superspace concept in the field of mineralogy. It appears that this concept can be applied for a more effective characterisation of the symmetry of crystal structures, and more generally of crystal chemistry and associated disciplines. Symmetry is also one of the fundamental characteristics, which is applied in mineralogical classifications. Therefore, the first application of the superspace approach in mineralogy concerns

the generalisation of crystal symmetry in higher dimensional (3+d)D superspace. We propose here to generalise the concept of Structure Type (ST), which is widely used in mineralogical classifications. It will allow combining some mineralogical families on the basic of a unique superspace group and a common basic structure model. On one hand, combined ST families can essentially simplify mineralogical classification; on the other hand, symmetrical and compositional relationships can be linked to the generation of minerals belonging to same family. The advantages offered by the (3+d)D ST concept can be illustrated with the description of the expanded glaserite, scheelite and palmierite (3+1)D mineralogical families.

Another aspect of the superspace approach, namely the concept of modulation, can be applied in mineralogy and further explored for the description of the polytypic families including mica minerals. It was shown that the so called modulation vector which can be obtained by experiment, is temperature dependent and each value corresponds to certain polytypes. This field of application is not yet tested in mineralogy, however, the palmierite-like polytypic family of synthetic compounds has been successfully described in superspace (Arakcheeva & Chapuis 2006).

The list of potential applications offered by the superspace approach seems to be very far from completed. We propose to explore further the concept of superspace and open new horizons of research in the field of mineralogy, petrography and geophysics.

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