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From the invalidity of the law of rational indices to the concept of superspace: A crystallographic excursion in the modulated world of minerals

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As well documented in a review paper on the modulated structures by Chapuis (2003), Goldschmidt et al. (1931), after optically studying more than 100 samples of the mineral calaverite ($AuTe_2$), declared the invalidity of the law of rational indices. What were the reasons leading them to draw such an extreme conclusion about the law of Haüy that had been accepted since 1784? Their declaration, however, was probably not generally accepted by the scientific community and their observations remained unexplained for the next forty years. The next major step in attempting to understand the results obtained by Goldschmidt et al. (1931) for calaverite occurred when Brouns et al. (1964) found anomalies in the diffraction pattern of synthetic Na_2CO_3. These authors were able to give the complete indexation of the pattern of the synthetic Na_2CO_3only by postulating an additional reciprocal dimension independent of the three usual ones. It was soon realised that the difficulties encountered by Goldschmidt et al. (1931) with the calaverite structure and the existence of satellite reflections were two aspects of the same phenomenon. From that point, the superspace theory, as developed by de Wolff et al. (1981), gave to crystallographers a unique tool for the generalization of the structural analytical methods to be applied to modulated structures. Any crystal structure requesting more than three integers to index its diffraction pattern can be described as a periodic object in superspace with dimension equal to the number of required integer (Chapuis, 2003). The structure observed in our real world is a three dimensional cut of the superspace description. In general, this cut is irrational and consequently the crystal is aperiodic. In recent years, the use of CCD and imaging plate systems considerably changed the sensitivity of data collection for modulated structures and, therefore, there was a need for further improvement of the methods. Today, several programs are able to solve and refine incommensurately modulated structures using the superspace approach.

In nature, it is uncommon to find minerals having strong and sharp incommensurate satellites that can be used for a multidimensional refinement. As a very clear example, the case of natural åkermanite, $Ca_2MgSi_2O_7$ (Bindi et al., 2001), which belongs to the melilite-group of minerals, will be shown in detail.The five-dimensional refinement carried out on this crystal shows that the displacive modulation of the atoms is mainly related to a variation of the Ca cation coordination.

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