

wüstite), calaverite, sulfosalts (cannizzarite, cylindrite, franckeite) or elements (e.g. sulphur under high pressure).

There are several underlying reasons for the modulations. They arise from, for instance, vacancy ordering, clustering of complex ions with different sizes and charges, rigid unit modes, intergrowths of domains with slight compositional variations, or internal misfits of different building units. In general, owing to the high flexibility in the chemical composition of minerals, occupational modulations are very frequent and play a prominent role in the formation of modulated mineral structures.

As an example the incommensurately modulated structure of nepheline ( $K_{0.54}Na_{3.24}Ca_{0.03}Al_{3.84}Si_{4.16}O_{16}$ ), which has been determined in superspace based on synchrotron diffraction data, will be presented in detail [1]. Displacive and occupational modulations in this mineral will be discussed and compared to those observed in other modulated minerals.

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#### Modulated molecular compounds

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Attempts to index the crystal faces of AuTe<sub>2</sub> alloys [1] following the law of the rational indexes are among the first reports suggesting the presence of aperiodicity in the crystalline structures. Around 1960's many examples of crystals presenting anomalies in the physical properties related with the lack of 3D periodicity were known [2-5]. In 1974 de Wolf came up with an entirely new superspace description for the modulated phases [6] and gave a common framework to interpret the observations. Most of the modulated compounds investigated up to date are inorganic salts or metal alloys in which the atomic modulations (displacive and occupational) could be interpreted in terms of frustration or competition, meaning that two or more mechanisms favour certain periodicities that are mutually incompatible [7]. Biphenyl, C<sub>12</sub>H<sub>10</sub>, is among the first modulated molecular crystal refined using the superspace approach [8]. Since that, many others modulated molecular structures have been identified and further investigated [e.g. 9-15]. One of the possible origins for the modulation in the molecular compounds is the interplay between molecular conformation and intermolecular interactions (crystal packing) [16-17]. However a better description of this interplay requires more experimental data highlighting the strength and the packing role of weak hydrogen and van der Waals interactions.

The relation between packing properties and modulation can be illustrated with the modulated molecular structures of the compound 4,4'-azoxydiphenetole. When it is crystallized below 356 K it presents a disordered modulated phase which is stable down to 20 K. Structural refinements indicate a high correlation between the displacements of the rigid molecular fragments – modulation – and the probability of finding them in different configurations – disorder. Disorder and modulation could be explained by a local competition between destabilizing and/or repulsive CH<sub>3</sub>...O, C<sub>ar</sub>H...π and CH<sub>3</sub>...π weak hydrogen interactions constrained by the C<sub>ar</sub>H...O bonds connecting the 4,4'-azoxydiphenetole molecules in the same layer.

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#### Complex ordering states in solid chemistry

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Solid states chemists, in their quest of original crystalline materials with potential applications, are often confronted with complex states somewhere in between the perfect order and the absolute disorder! Numerous materials considered as disordered in the literature belong in fact to this border area. The recent improvement of the diffraction's techniques (mainly the development of the 2d detector) allows the well informed crystallographers to reveal the true nature of such materials. Among the published disordered compounds, some of them are characterized by aperiodic structures. In this case, additional satellite reflections in irrational positions with the basic lattice can be now observed in the reciprocal space: they are characteristic of incommensurate modulated structures. Using these new data and a superspace approach, it is often possible to go past the average "disordered" structure: the structural complexity can be, at least partly, determined.

