

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 AuTe₂ 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, C₁₂H₁₀, 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 CH₃...O, C_{ar}H...π and CH₃...π weak hydrogen interactions constrained by the C_{ar}H...O bonds connecting the 4,4'-azoxydiphenetole molecules in the same layer.

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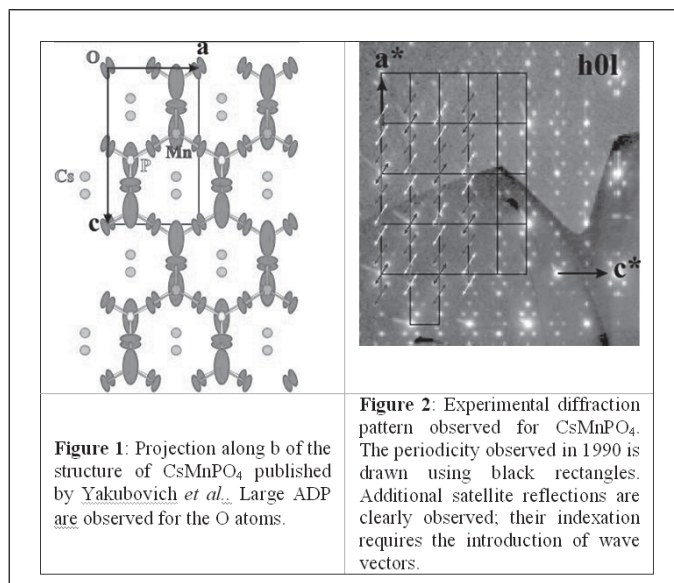
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Complex ordering states in solid chemistry

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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.



This purpose will be illustrated by two examples. The disorder previously evidenced either by the splitting of atoms over different sites in tunnels of $\text{Sr}_6(\text{AlO}_2)_{12}\text{Bi}_2\text{O}_3$ [1] or the large ADP of oxygen atoms of CsMPO_4 [2] (Fig. 1) can be elucidate just by observing satellite reflections (Fig. 2) and then solving the modulated structure [3] using superspace formalism.

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Relationship of the aperiodic structure to the nanostructure

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This paper aims to evidence that some typical aperiodic crystal materials, such as the composite and the modulated ones, show a *nanostructured material and just this nanostructure conditions the unique properties of the aperiodic material*. The fragments, as the “basic units”, that make up the material are nanoscaled and *aperiodically* arranged with respect to each other. To the preparation of such nanostructure, the consolidated and fashioned fragments (as the nanoparticles or nanolayers) can be composite or modulated in a bulk material. This process is widespread in biology with the variety of self-assembly [1].

The key problem is, the nanoworld is of *quantum nature* that creates the peculiar dynamics of the odd electrons (i.e. the active electrons, they show the unpaired spins) in the nanostructured material [2, 3]. And just this peculiar electron dynamics breeds the prominent features of the aperiodic material. For studying these effects, Electron Spin Resonance (ESR) can offer an especially efficacious help means.

From the experimental and theoretical results with ESR in combination with other methods, some peculiarities of dynamics of electrons in the real aperiodic materials can be summarized as follows:

1) The active electrons in the aperiodic structure can be considered as the Quasi-Free Electrons (QFEs) moving in a Nano Resonant Cavity (NRC) with nanoparticles or in a Nano Wave Guide (NWG) with nanowires and nanolayers of the nanoscaled Short-Range Order.

2) The QFEs must obey a “Compressed Distribution” as a normal Gauss form of the state density. This very outstanding peculiarity springs from the resonant character of the NRC and NWG and can strongly influence the ability of the aperiodic material to absorption and emission of radiation.

3) The NRC and NWG can essentially favour the strong superexchange interactions of their QFEs. Thereby, two types of the spin coupled pairs (the Antiferromagnetic pair and the Ferromagnetic pair) can simultaneously occur and the [2A-2F] fivefold clusters can be spontaneously formed. This aperiodic structure can bring out an energy minimum, and therefore a stable existence of the fivefold clusters.

4) The spin coupling brings about different spin gaps of the QFEs in the NRC and NWG, thereby can cause the peculiar conductivity or the superconductivity of the aperiodic materials.

5) The interaction of the QFEs with the surroundings (Jahn-Teller effect) can generate a strong local crystal field of low symmetry in the aperiodic structure, especially in the aperiodic structure of the living body.

When the scale of the fragments (particles, wires or layers) extend

out of the nanorange, the material becomes polycrystalline and its above mentioned peculiarities will disappear.

As illustrative examples, the results on *Composite Fivefold Aperiodic Structure of Dental Enamels* [4] and *Superconducting Nanomechanism in YBCO Compounds* [5] are briefly analysed.

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Twenty years of the crystallographic information framework

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The Crystallographic Information File (CIF) format was adopted by the International Union of Crystallography (IUCr) as the standard for exchanging and archiving crystallographic information in 1991 [1] and has continued to be developed actively during the past two decades.

The initial specification used the Self-Defining Text Archive and Retrieval (STAR) format developed as a universal exchange mechanism [2] and subsequently used in a number of other scientific fields including botany, chemistry and NMR structure determination. Later developments including machine-readable dictionaries of data identifiers with associated attributes helped to separate the semantic content of CIF from its syntactic structure, allowing easy interchange with XML or other widespread formats. Work has continued to extend the dictionary definition language to include information about the permitted data content in a manner that computers can process directly. Latest work focuses on specifying algorithmic relationships between individual data items.

The result has been an information system that includes its own recipes for computational validation of related data items. This has allowed CIF to be used in electronic publishing and in database applications, where validation, integrity checking and format transformations can be performed automatically and with no or little information loss. Consequently, CIF underpins the entire publishing workflow of IUCr journal articles reporting crystal structures [3], and is an important intermediary in the management of the curated structural databases such as Protein Data Bank [4] and Cambridge Structural Database.

CIF separates semantics from syntax to a large degree, and has a rich granularity in its item descriptions. It adopts a uniform approach that treats experimental data and associated descriptive information (often called ‘metadata’) in the same way. It has come to be accepted as a standard across the entire field of crystallography that can handle raw image data, information about structure solution and refinement, the positional and displacement parameters of a derived structural model, and all aspects of an associated publication. In all these ways, it serves as a model for effective information flow – a model that is increasingly being used for case studies by other disciplines seeking to improve their data management strategies [5]. Predating the Web and XML, CIF remains at the leading edge of scientific information management systems.

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