Keynote Lectures

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Magnetic neutron crystallography - commensurate and incommensurate structures

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Magnetic crystallography — description of crystal magnetic structures with the help of crystallographic concepts — is gradually acquiring the features of a full-fledged science. Physical models of an ordered magnetic state in crystals have been formulated and tested. The necessary experimental equipment based primarily on the diffraction of slow neutrons has been constructed and successfully operate. The main stages of determining the magnetic structure including the determination of the propagation vector of the structure, values and orientations of atomic magnetic moments have become clear. Finally, the algorithms for precise analysis of magnetic experimental diffraction data have been designed and implemented.

Quantum models of magnetism are based on the concept of exchange interaction, the main of which for the consideration of the magnetic structure of crystals being the Heisenberg-Dirac-Van-Vleck model of interaction of localized magnetic moments. Magnetic structural experiments are mainly carried out on steady-state neutron sources using cold neutron beams. Accessible ranges of temperature and external pressure are very broad — a diamond anvil cell makes it possible to perform experiments at a pressure as high as 30 GPa and a temperature as low as 0.1 K. The TOF technique at high-flux pulsed neutron sources gives rise to some new opportunities. In particular, at TOF neutron diffractometers it is possible to register diffraction patterns with a relatively high resolution over a very wide range of d-spacings, which allows simultaneous refinement of both atomic and magnetic structures. The role of other nuclear techniques remains to be secondary, though μSR and Mössbauer spectroscopy could be very useful in complicated cases, especially if the local features of the magnetic structure are important.

Of the two possible ways of crystallographic description of magnetic structures — "Symmetrical" based on Shubnikov or color groups and "Representative" based on irreducible representations of Fedorov groups — the center of gravity is gradually shifting towards the latter. This is manifested in the introduction to the daily practice of several software packages that allow very clear selection of magnetic structures, which are correct from the symmetrical point of view, and analysis of their consistency with the experimental data. Moreover, the approach based on irreducible representations secures a uniform analysis of the magnetic structure regardless of whether it is commensurate or incommensurate. Discussion of this particular aspect is the main content of the report.

A few examples of neutron diffraction data analysis selected from the practice of recent years will be discussed in detail to illustrate the relationship of crystallographic and physical aspects in the formation of specific magnetic structures (commensurate and incommensurate).

Keywords: magnetic, neutron, diffraction

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XDX - An initial solution to crystallization

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Crystallization is somewhat hidden in the pathway to a structure, and yet is an absolute requirement for crystallography. The numbers from the structural genomics initiatives show that the major bottleneck in the determination of biological structures is the production of diffraction quality crystals. Given this, there has been a great push into automation in order to streamline the process of crystallogenesis. Despite a massive investment in robots the success rate of crystallisation hasn't changed dramatically in 30 years – we just do more of it now.

What do we need to do in order to improve? Learning from past experiences, sharing data between crystallization centres and focusing on extracting maximum information from each experiment would all be good steps. With these goals in mind, we have undertaken to develop a semantic representation of the crystallization domain – an ontology which would provide the underpinnings for data exchange and analyses.

Keywords: crystallization, data, ontology

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Crystal engineering. From molecules to crystals

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The essential question in crystal engineering is: Given the molecular structure of an organic compound, what is its crystal structure? The difficulty in answering this question lies in that a crystal structure is an emergent property and that it depends on molecular structure in non-obvious ways. The basis of molecular chemistry is the functional group. Molecular functionality is, however, a very poor indicator of supramolecular properties, like a crystal structure. Therefore prediction of a crystal structure requires analysis at a higher level. This higher level is provided by the concept of the supramolecular synthon (S) which is an assembly of molecular functionalities (M1, M2, M3) that encapsulates kinetic information. A synthon is a structural unit that is found often enough so that one may reasonably predict that an occurrence of say M1, M2, M3 in a molecule, with or without the simultaneous occurrence of say M4 and M5, will preferentially result in the formation of synthon S1, in preference to say S2 and S3. The concept of the synthon is a simplifying one. One tries to identify certain critical regions of the molecule that will influence and determine a stable crystal structure.

The synthon goes, however, beyond being a static descriptor of crystal structure. It is not a pattern, a building block or a motif, all terms that are used often enough in the crystal engineering literature. The synthon is a kinetic descriptor, that accurately reflects modularity. In its repeated appearance in crystal structures is a hint that there are preferred strong and weak intermolecular interactions that serve as kinetic routes to crystal structures. This is in contrast to the most stable crystal structures that can be formed for a given molecule, in the limit the global minimum or the thermodynamic structure. The latter structures minimize energy and ideally, optimize close packing and maximize crystal density. They are the kinds of structures that emerge in computational predictions of unknown crystal structures. So we have