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Applications of TEM in the study of incommensurately modulated compounds

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In the study of incommensurate modulated compounds, transmission electron microscopy (TEM) is an invaluable tool for characterisation. In cases where large single crystals are not available, TEM will still allow to clearly distinguish the satellite reflections. This allows to determine the superspace symmetry and modulation vector. Several examples will be presented of materials whose structure could only be solved by first turning to TEM. First, $AxMnO_2$ ($x<1$) tunnel structures will be presented. The tunnel walls are built from rutile-type chains of edge-sharing MnO_6 octahedra forming a variety of tunnel structures by being combined in different manners. The A-cation strings in the tunnels can contain ordered vacancies and, along with a displacement of the A-cations, this results in modulated structures. The shape of the tunnels and the order of the A-cations vary depending on the size of the A-cation and the A/Mn ratio, linking the modulation to the composition.[e.g. 1-2] The second example is the new family of perovskite based structures having crystallographic shear planes. This requires a cation with a lone electron pair in the A-position, such as Pb^{2+}. The crystallographic orientation of the shear planes can be controlled through the choice and amount of other A-cations substituting for Pb, resulting in a series of incommensurately modulated materials. The building principles, features of the diffraction patterns and chemical compositions of this series will be shown as found in different variants of '$(Pb,A)_2Fe_2O_5$'. [3-4]

[1]A.M. Abakumov et al. Chem. Mater.19(2007)1181
[2]J. Hadermann et al. Chem. Mater.18(2006)5530
[3]A.M. Abakumov et al. Ang.Chem.Int.Ed.,Volume 45,40(2006)6697
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Super space formalism to crack complex codes in material chemistry

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Critical parameters such as non stoichiometry are essential for the formation of numerous phases in material chemistry. But they are often difficult to identify since hidden by incommensurate modulations, shearing mechanisms or structural disorders. Structural determination of these complex phenomena using the super space formalism (SF) is particularly efficient to reveal the hidden parameters. This assumption is obvious for incommensurate structures. The example of hollandite exhibiting strong modulations leading to an ordering of guest ions / vacancies in the host is given. The efficiency of the SF is more obscure for compounds exhibiting either shearing or disorders. In both cases, a new interpretation of the direct and of the reciprocal space is request. The structure of materials resulting from shearing mechanisms can be classically solved. The observation of a subperiodicity and the use of SF provides a more global overview of the structure. The role of the composition as driving force for the shearing mechanisms and the relations between different phases can be then revealed as illustrated by the study of $Bi_{14}Sr_{21}Fe_{12}O_{61}$ and $Bi_{12}Sr_{18}Fe_{10}O_{52}$. For disordered materials only the average structure can be obtained; the disorder prevents an accurate determination of the local atomic environments. However the observation for some compounds of diffuse scattering can lead to an insight of the local order of the real structure. In this purpose an ideal diffraction pattern can be designed by replacing the diffuse scattering by punctual reflections. The ideal ordered structure, determined from these artificial data using the SF, compared with the average one provides an accurate description of the real local structure. The study of $NH_4Fe_2(PO_4)_2$ will illustrate our purpose.

Keywords: disordered structures, incommensurate modulated structures, superspace symmetry

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Long-period structures in the superspace formalism: From pyrrhotite to modular structures

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The superspace formalism (SF) was originally developed for the structural analysis of incommensurate structures. Several years later, it was also applied in the study of composites and quasicrystals. But, in the last years, the SF has been revealed as a very efficient tool to describe periodic crystals with large unit cells when the 3-dimensional structure possess, on average, a smaller sub-periodicity or it is composed of several subsystems with smaller sub-periodicities. The application of the SF is particularly interesting in series of layered phases with composition-dependent stacking sequences because, typically, a unique superspace model describes correctly the structure of all the compounds. In these cases, the atomic domains, which represent the atoms in the superspace, are given by step-like crenel functions that, usually, fulfil the so-called closeness condition. This condition implies the existence of a direct relation between the modulation parameter(s) and the composition. There is another kind of long-period crystals, frequently observed in the mineral world, called modular structures. Usually described as the periodic juxtaposition of two or more types of modules, often, each ideal modulus has an internal sub-periodicity. In some cases, different modules are related by a symmetry operation that does not belong to the space group of each of the modules. Recent examples of the application of the SF to different kinds of structures are included, starting with the pyrrhotite (Izaola, Z., Gonzalez, S., Elcoro, L., Perez-Mato, J.M., Madariaga, G., Garcia, A. (2007) Acta Cryst B63, 693-702.) and, as an example of a modular structure, the lillianite family (Perez-Mato, J.M., Elcoro, L., Friese, K., Petricek, V., Balic-Zunic, T., Arnskov Olsen, L., to be published)

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