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Precise absolute structure determination for light-atom structures

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In an absolute structure determination one absolute structure is refined competitively against the inverted alternative. The result is expressed by the Flack parameter $x(u)$, which for absolute configuration determination can be interpreted as the mole fraction of the alternative enantiomer in the crystal [1]. The physical range of x is 0 to 1; Flack and Bernardinelli have shown that even if the bulk material is known to be enantiopure the standard uncertainty (u) should be less than 0.1 before any firm conclusions can be drawn [2].

The likely success of an absolute structure determination can be gauged using the *Friedif* parameter [3]. If *Friedif* has a value of about 80 or more routine absolute structure determination should present little problem. Light atom structures may have values of *Friedif* of 30 or less even for Cu-K α radiation, and Flack and Bernardinelli's criterion has proved to be extremely demanding for such cases. Two refinement strategies will be described which can improve the u to 0.1 or less for such structures.

One method is based on the quantity

$$D(\mathbf{h}) = \frac{I(\mathbf{h}) - I(-\mathbf{h})}{I(\mathbf{h}) + I(-\mathbf{h})} = (1 - 2x) \frac{F^2(\mathbf{h}) - F^2(-\mathbf{h})}{F^2(\mathbf{h}) + F^2(-\mathbf{h})}$$

The term based on $I(\mathbf{h})$ and $I(-\mathbf{h})$ and its standard uncertainty can be calculated from a single crystal X-ray diffraction data set. The term based on $F^2(\mathbf{h})$ and $F^2(-\mathbf{h})$ can be calculated from the model. It is therefore possible to write out a set of restraints based on observed and calculated values of $D(\mathbf{h})$ and apply these in an absolute structure refinement. Systematic errors in the intensities, such as absorption, tend to cancel out (in an average way) so that measured values of $D(\mathbf{h})$ should be more accurate than the values of the measured intensities.

The second method is based on *leverage analysis*, which yields quantities which measure the influence that observations have on the precision of a specific parameter. [4] A weighting scheme has been developed where data which strongly influence the Flack parameter are systematically up-weighted.

Both methods yield significantly more precise values of the Flack parameter than conventional refinement. For example when a data set was collected for L-alanine (*Friedif* = 34) with Cu-K α radiation at 100 K, conventional refinement yielded a Flack parameter equal to 0.12(21), whereas the restrained refinement yielded a value of 0.00(8). A refinement based on the leveraged weighting scheme yielded $x = -0.02(5)$. In the case of a hydrocarbon with *Friedif* = 9 a value of $x = 0.07(10)$ was obtained.

Both methods carry the advantage that the Flack parameter is allowed to refine along with all the other parameters, so that its standard uncertainty reflects correlations present in the refinement.

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Anion-deficient perovskites modulated by periodic translational interfaces

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Although the perovskite-related structures have already been investigated extensively for many years, some blank spots in this field have still not been unraveled. Here I present a new family of anion-deficient perovskite-based compounds containing an easily polarizable A cation with a sterically active lone electron pair, where the parent structure is periodically modulated by translational interfaces with properties similar to those of crystallographic shear (CS) planes [1, 2]. The oxygen content in the anion-deficient perovskites $(\text{Pb,Bi})_{1-x}\text{Fe}_{1+x}\text{O}_{3-y}$ can be varied over a wide range through a long-range-ordered arrangement of the (CS) planes, resulting in incommensurately modulated structures. Based on the results of electron diffraction, high-resolution scanning transmission electron microscopy and neutron powder diffraction a superspace model was constructed describing a periodic arrangement of the CS planes of any arbitrary orientation. The superspace description is based on compositionally-dependent constructions of discontinuous atomic domains for the layer sequences of two basic low-index CS planes subsequently “merging” them in appropriate ratio into a single superspace model for the CS planes of desired orientation. The refinement of displacive modulation parameters revealed the antiferroelectric nature of the structure related to antiparallel orientation of the lone electron pair domains on Pb^{2+} and Bi^{3+} at both sides of the CS planes.

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Minerals in superspace

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Modulated structures are frequently observed in mineral systems. Their existence is usually restricted to certain pressure/temperature conditions and often depends on the composition. Thus minerals of the same group may show modulations if they are from one type location, while they have normal structures, if they are from a different location, where the formation conditions were different.

Some examples of minerals exhibiting modulated structures are: framework aluminosilicates (e.g. plagioclase, nepheline, sodalites), silica polymorphs (e.g. quartz, tridymite), layered aluminosilicates (e.g. melilites, antigorite, fersnoite), iron oxides and sulfides (pyrrhotite,

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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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.

