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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 Bernadinelli'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 that 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 $(Pb,Bi)_{1-x}Fe_{1+x}O_{3-y}$ 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 alumosilicates (e.g. plagioclase, nepheline, sodalites), silica polymorphs (e.g. quartz, tridymite), layered alumosilicates (e.g. melilites, antigorite, fresnoite), iron oxides and sulfides (pyrrhotite,