JANA2006 AS A TOOL FOR SOLUTION AND REFINEMENT OF NON-STANDARD CRYSTAL STRUCTURES

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The experimental techniques used in a standard diffraction experiment allow nowadays much deeper insight into crystal structure details than in the past. CCD cameras are able to scan in reasonably short time a large portion of the reciprocal space. Thus the problem how to collect sufficient number of systematically weak reflections such as satellites for modulated crystals is considerably reduced. This opens possibility to study difficult modulated structures at very reasonable resolution and redundancy.

Modulation in crystals can substantially affect crystal properties and they are very often connected with phase transitions. As it has been shown in pioneer's works of de Wolff, Janner and Janssen [1] modulated crystals, which have not anymore classical three dimensional translation symmetry, can be described in higher dimensional space - superspace - as generalized crystal with translation symmetry relocated in the higher dimension. Since this discovery in eighties of the last century the classical techniques available for solution and refinement of regular structures have been eventually generalized to aperiodic ones making structure analysis of modulated structures almost a routine task. An important progress in the last years is connected with new solution technique, charge flipping algorithm, which has been also generalized to aperiodic crystals and implemented to the program Superflip [2].

The program system Jana2006 [3] contains all tools necessary for refinement and interpretation of modulated structures. For solution the above mentioned method of charge flipping has been used and the program Superflip was directly connected with Jana2006. Its power will be demonstrated with already published structure of $KAsF_4(OH)_2$ [4].

The modulation functions describing periodic perturbation of the basic structural parameters (atomic occupancies, positions and ADP's) can often exhibit discontinuities. For this reason discontinuous functions called crenel and saw-tooth function have been introduced [5]. They are used to model discontinuity in the crystal and they can be combined with additional continuous modulation. Their usage has been recently facilitated by introducing of Legendre polynomials for positional and ADP modulation. This approach overcomes the tricky problem of missing orthogonalism due to discontinuity which complicated combination of discontinuous and harmonic functions. With Legendre polynomials seamless switching between continuous and discontinuous functions is possible as well as between crenel and sawtooth function.

Another problem complicating structure determination and refinement is twinning. The computing system Jana2006 allows refinement of structures having complete overlap (*i.e.* meroedric twins and pseudo-meroedric twins with negligible oblique) or partial overlaps of diffraction spots. The number of twin domains is arbitrary, the program uses either twinning matrices or HKLF5 format. The method has been recently generalized for mutliphase single-crystal samples composed from related, but generally different, phases. It can be used even in cases when one of phases in modulated and the second one not [6]. Such an option is especially important for samples of natural minerals and in analysis of phase transitions.

The newest version of the system Jana2006 can also use and combine several data sets from different sources, for instance powder and single crystal data either from X-ray diffraction with different wave lengths or from neutrons. This approach makes possible to refine structural details with different contribution to structure factors, for instance anharmonic ADPs and charge densities, against joint data sets based on X-ray and neutron diffraction.

References

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