Advances in solution of modulated structures reflected by Jana system

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Abstract. The latest development in the x-ray diffractometers makes modulated structures more frequent and accessible than ever before. The last version of Jana software, Jana2006, contains improvements facilitating solution of modulated structures for non-specialists. The initial structure model, including modulations, is now created in communication with the charge flipping program Superflip. Combination of discontinuous functions with position modulation does not require any more orthogonalization procedure because position modulation is newly expressed by Legendre polynomials. For difficult tasks Jana2006 adds possibility to combine data sources, including powder and single crystal data, regardless on the source of diffraction (x-ray, synchrotron, neutron). This feature helps in refinement of magnetic structures. They have obtained full support in Jana2006, including tools for testing magnetic symmetry and representative analysis. Both nuclear and magnetic structures can be modulated and the can be jointly refined against one or more data sets.

1. Introduction
In the last few years we have seen rapid progress in home laboratory instruments for x-ray diffraction. With sensitive area detectors and new x-ray optics overlooking of satellites has become almost impossible and number of known modulated structures has been growing rapidly. Programs for modulated structures are now used by larger number of crystallographers than ever before and many of them are not specialists for aperiodic structures. The new demand on the computing tools is accessibility and friendliness retaining at the same time all possibilities for complicated problems. This direction is reflected in Jana2006 system [1] by including the charge flipping method for ab initio solution of modulated structures and by better support of often used discontinuous functions.

On the other hand, the progress in the experimental possibilities enables solution of more complicated structures. During the last years there was growing interest among the users of Jana2006 to refine jointly neutron diffraction data and synchrotron data, especially for the purpose of the magnetic structures refinement. Jana2006 reflects also this kind of requests by introducing possibility to jointly refine a structure against almost any combination of diffraction data including combination of powder and single crystal data. The support for magnetic structures has been added recently, too.

2. Integration of charge flipping
Charge flipping [2] has become a new alternative for solution of the phase problem. The input for charge flipping is diffraction data only; neither symmetry information nor chemical composition is
required. Charge flipping yields three or more (depending on number of indices) dimensional electron density map. In order to get the structure model the electron density map must be interpreted. For standard structures it may reveal atomic positions, disorder and anharmonic features, for modulated structures the map contains atomic domains which can be described in terms of basic atomic positions and modulation functions.

The importance of charge flipping in the field of modulated structures is much larger than for standard structures because this is the only well established method which can solve a modulated structure without preliminary knowledge of the average structure. This is especially useful for strongly modulated structures where finding of the average structure may be difficult and a refinement of modulation functions from arbitrary small displacements may be misleading.

Jana2006 communicates with the charge flipping program Superflip [3] by the way that it prepares input files, executes Superflip as an external program and interprets the resulting electron density map in terms of basic atomic positions and modulation functions. For structures where harmonic position modulation dominates one can immediately start refinement of the structure found from the charge flipping. For discontinuous functions, however, the starting parameters (centre and width) must be found manually using sections through the electron density map from charge flipping.

Superflip can also search for symmetry in the resulting electron density map. This can be used as an independent symmetry check in addition to the classical methods based on R_{int} and systematic extinctions.

3. Discontinuous functions in Jana2006

Six of the ten latest modulated structures published in Acta Crystallographica B [4-13] use discontinuous functions, either crenel or sawtooth, for the description of the structure model. Apparently discontinuous functions are no longer reserved for special cases. They should be understood as a basic tool and receive a corresponding support that would allow their utilization by non-specialists.

Discontinuous functions were introduced in 1990 (sawtooth function, [14]) and in 1995 (crenel function, [15]) in order to facilitate refinement of structures with abrupt modulation changes of position and occupation. Crenel function describes modulation of occupancy by defining an interval in x_{4} where the corresponding atom exists. It is defined by the width and the centre, both of them can be refined. The sawtooth function combines crenel modulation of occupancy with linear modulation of position and it is therefore defined by the width, the centre and the slope of the line along x_{1}, x_{2} and x_{3} axes of the basic unit cell. Both crenel and sawtooth functions can be combined with harmonic position modulation.

In previous versions of Jana software usage of crenel or sawtooth function required a lot of user interaction. The centre, width and (for sawtooth) slope had to be found in the Fourier sections x_{1}-x_{4}, x_{2}-x_{4} and x_{3}-x_{4}, respectively. The combination of crenel or sawtooth functions with harmonic modulation usually required to use orthogonalization procedure [15] in order to make the modulation functions mutually orthogonal in the restricted interval of x_{4} corresponding to the width. This semi-automatic procedure calculated – based on the centre and width of crenel – selection rules defining which sine and cosine terms of the harmonic modulation function can be used in the refinement. The orthogonalization procedure had to be repeated after any significant change of the width or the centre of crenel or sawtooth function. The change in selection rules often destroyed the structure model. Finally, since there is no CIF definition for selection rules, refinement could not be repeated from the publication CIF files.

Instead of harmonic modulation functions, Jana2006 combines crenel functions with Legendre polynomials [16]. The Legendre polynomial P_{n}(z) can be defined by equation

\[ P_{n}(z) = \frac{1}{2^{n} n!} \frac{d^{n}}{dx^{n}}(x^{2} - 1) \]
The Legendre polynomials are orthogonal over the interval (-1,1), i.e. they satisfy the equation

\[ \int_{-1}^{1} P_n(x)P_m(x)dx = \frac{2}{2n+1} \delta_{mn} \]  

(2)

The original crenel interval \((x_{40} - \Delta/2, x_{40} + \Delta/2)\) can be transformed to the interval (-1,1) by

\[ \xi = 2(x_4 - x_{40})/\Delta, \]  

(3)

where \(x_{40}\) and \(\Delta\) are the centre and width of the crenel function, respectively. For a full interval \(\Delta = 1\), i.e. \((x_{40} - 1/2, x_{40} + 1/2)\), this approach can be used, too.

Thus, the Legendre polynomials can combined with crenel function without any additional orthogonalization procedure which facilitates usage of discontinuous functions and leads to more stable and less correlated refinement. For the description of modulation the odd and even polynomials are coupled, \(P_1\) and \(P_2\) forming the first modulation wave, \(P_3\) and \(P_4\) the second wave etc. By this way an analogy is achieved with the original expressions for modulations by harmonic waves. For instance, for position modulation we get

\[ r_\nu = r_{\nu,0} + \sum_n U_{in}^s \sin(2nx_4) + U_{in}^c \cos(2nx_4) \]  

(4)

when harmonic waves are used, and

\[ r_\nu = r_{\nu,0} + \sum_n S_{in}^o P_n^o [2(x_4 - x_{40})/\Delta] + S_{in}^e P_n^e [2(x_4 - x_{40})/\Delta] \]  

(5)

with Legendre polynomials. In the equation (4),(5) \(r_{\nu,0}\) is the basic position of the atom \(\nu\); \(U_{in}^s\) and \(U_{in}^c\) are Fourier amplitudes of the sine and cosine term, respectively, of the \(n^{th}\) modulation wave of the atom \(\nu\); “o” and “e” superscript stands for odd and even member of the Legendre polynomial forming the modulation wave.

The first order term \(P_1\) defines a simple linear function at interval \((x_{40} - \Delta/2, x_{40} + \Delta/2)\), which corresponds to a sawtooth modulation. Thus there is no more reason for treating sawtooth and crenel separately; crenel combined with the first Legendre modulation wave acts always like a sawtooth function with inclination encoded in the first three modulation parameters. For example, a sawtooth function defined over the whole interval of \(x_{40}\) can be expressed as a crenel function defined over the the same full interval and combined with Legendre modulation wave (figure 1). An article explaining in detail the topic of Legendre polynomials used for description of modulation is under preparation.
Figure 1. Sawtooth function created like combination of crenel function \( x_0 = 0.04, \Delta = 1 \) with positional modulation expressed by Legendre polynomials. (a) No combination; (b) 1st order polynomial, (c) 1st and 2nd order polynomial; (d) 1st, 2nd, 3rd and 4th order polynomial. The resulting modulation function is overlaid with the corresponding Fourier maximum. The horizontal dotted line indicates position of the centre of the crenel function.

4. Magnetic structures and joint refinement

At very low temperatures some magnetic materials undergo magnetic phase transition due to ordering of magnetic moments. This ordering leads to the presence of magnetic reflections that can be observed in the diffraction pattern with help of neutron diffraction. The magnetic structure factor can be described like

\[
\tilde{F}_M(h) = p \sum_i f_i(h) T_i(h) \tilde{S}_i \exp(2\pi h \cdot r_i),
\]

where \( f_i \) is magnetic form factor, \( T_i \) is temperature factor, \( \tilde{S}_i \) is magnetic moment and \( r_i \) is an atomic position. The reason for the growing interest among users of Jana2006 to use this program for refinement of magnetic structures is due to the fact that the distribution of magnetic moment over the nuclear structure can be described by modulation wave

\[
S_i(x_4) = S_{i0} + \sum_{n=1}^{N} [S_{i\sin}(2\pi n x_4) + S_{i\cos}(2\pi n x_4)],
\]

where \( S_{i0} \) is the basic magnetic moment, \( S_{i\sin} \) and \( S_{i\cos} \) are amplitudes of the sin and cos term of the n-th modulation wave, respectively. Thus the tools developed for modulated structures could be generalized and used also for magnetic structures.

The magnetic reflections contribute to the diffraction pattern by the way that their intensities are summed with intensities of reflections corresponding to nuclear structure. From the calculation point of view we can consider a magnetic sample to be a multiphase consisting of nuclear and magnetic phase. From the experimental point of view the data measured under the temperature of the magnetic phase transition are often short strips of neutron powder diffraction data that nicely show the magnetic reflections but their quality is not sufficient for precise determination of the nuclear structure. Therefore a combination seems to be very practical of the powder neutron data with a complete measurement, not necessarily using neutrons, done for the purpose of the exact determination of the crystal structure. Apparently introducing of magnetic structures into the Jana system should be
accompanied with a new possibility of joint refinement of the same structure against different diffraction data, of a multiphase structure against the same diffraction data or – generally – of a multiphase structure against several diffraction data.

The latest version of Jana2006 contains complete set of tools for investigation and determination of magnetic structures. Magnetic symmetry can be defined with magnetic space or superspace group symbols using comma for the time inversion. A tool for testing magnetic symmetry allows calculating global magnetic moment pertinent to the selected symmetry symbol and immediate comparing the extinction rules for magnetic reflections (following from the chosen symmetry) with the experimental diffraction pattern. Representative analysis can be generated for arbitrary dimension and the resulted representations can be unambiguously assigned with the magnetic symmetry symbol. The later required some theoretical investigation which will be soon published in a separate article. The magnetic structure, either modulated or three dimensional, either incommensurate or commensurate, can be refined together with nuclear structure which can be also modulated, using the same or different diffraction data.

The impulse for introducing joint refinement into Jana system came from the field of magnetic structures but finally the method works for any combination except electron diffraction data (figure 2). The most useful combination remains joint refinement against neutron and synchrotron or x-ray data. The minimized function for $n$ single crystal phases and $m$ powder phases can be expressed like

$$
S = \sum_h w_{h,1} \left( F_{\text{obs},1}(h) - F_{\text{calc},1}(h) \right)^2 + \ldots + \sum_h w_{h,n} \left( F_{\text{obs},n}(h) - F_{\text{calc},n}(h) \right)^2 + \\
\sum_i w_{i,1} \left( I_{\text{obs},i,1} - I_{\text{calc},i,1} \right)^2 + \ldots + \sum_i w_{i,m} \left( I_{\text{obs},i,m} - I_{\text{calc},i,m} \right)^2,
$$

(8)

where $F_{\text{obs}}(h)$ and $F_{\text{calc}}(h)$ are observed and calculated structure factors while $I_{\text{obs},i}$ and $I_{\text{calc},i}$ are observed and calculated intensities of the powder profile point $i$. For joint refinement against combination of powder and single crystal data the weight $w$ of a structure factor or of a profile point is of critical importance because one measurement should not be over weighted by another measurement. The partial experiments should be done carefully and the weighting scheme must be strictly derived from the counting statistics.

Another problem in joint refinement comes from different meaning of “temperature” parameters for neutron and x-ray diffraction data. Jana2006 introduces an overall atomic displacement parameter ADP which scales the ADP for partial data sets.

**Figure 2.** The flowchart illustrating possibilities of joint refinement with Jana2006. Single crystal domains have the same structure while single crystal phases have different structures. Magnetic structure is understood as a special kind of phase.
Up to now only a few examples exists of successful application of joint refinement of powder and single crystal data but they have not been published yet. The same situation is for magnetic structures. Refinement of coexisting single crystal phases with jana2006 has been reported in [17].

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