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orientation matrix and modulation vector(s)**

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NADA – a computer program for the simultaneous refinement of orientation matrix and modulation vector(s)

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NADA is a computer program for the simultaneous refinement of the components of the orientation matrix and the components of up to three modulation vectors by the method of least squares. Using the spatial peak positions and the orientation matrix of the main reflections from a single-crystal diffraction experiment and rough estimates of the modulation vector(s) components, *NADA* re-indexes the peaks (main and satellite reflections) with integers in higher dimensions ($hklm_1$, $hklm_1m_2$ or $hklm_1m_2m_3$, respectively) and refines the orientation matrix and modulation vector(s) components from the observed peak positions. Standard uncertainties on all refined parameters are calculated analytically.

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1. Introduction

In addition to main reflections, diffraction patterns of modulated crystals also show satellite reflections. If the modulation is strong or if the modulation is two- or three-dimensional, the number of satellite reflections can become quite important and the measurement of all reflections (several tens of thousands) can become quite time consuming with a conventional point detector. Two-dimensional detectors (CCD detectors and image-plate detectors) provide a fast and common way for the intensity measurement of modulated crystals.

Very often the current commercial diffractometer software is not properly adapted to analyse the data in higher dimensions for the following reasons. Firstly, it offers either no possibility to refine the components of the modulation vector(s) or only the possibility to refine the components of a single modulation vector per step as a function of the orientation matrix (using $hklm_1$, $hklm_1m_2$ or $hklm_1m_2m_3$ with $m_1 \neq 0$, $m_2 \neq 0$ and $m_3 \neq 0$, respectively). Secondly, the orientation matrix, from which the cell parameters are derived, is based on the main reflections only ($hkl0$, $hkl00$ or $hkl000$, respectively), in analogy to non-modulated crystals. Neglecting the contribution of satellite reflections introduces some bias in the refined parameters. In the *International Tables for Crystallography*, Vol. C (Janssen *et al.*, 1992), satellite reflections are defined as

$$\mathbf{H}_{\text{Satellite}} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m_1\mathbf{q}_1 + m_2\mathbf{q}_2 + \dots + m_d\mathbf{q}_d \quad (1)$$

with

$$\mathbf{q}_i = \alpha_i\mathbf{a}^* + \beta_i\mathbf{b}^* + \gamma_i\mathbf{c}^* \quad (2)$$

and not only as

$$\mathbf{H}_{\text{Satellite}} = m_1\mathbf{q}_1 + m_2\mathbf{q}_2 + \dots + m_d\mathbf{q}_d. \quad (3)$$

For crystals with a small modulation and weak satellites of first and perhaps also second order, this approach might be acceptable, since there are few satellite spots available. For crystals with strong modulations and satellites up to high order, the current approaches mean an important loss of valuable information for the cell parameters and for the modulation vector(s) components.

The main motivation for writing the program was to fill this gap. *NADA* can handle up to three modulation vectors (for one-dimensional, two-dimensional and three-dimensional modulated crystals, respectively). It refines simultaneously their components along with the orientation matrix in the same least-squares refinement cycles, using the full set of reflections for each refined parameter, without discrimination between main and satellite reflections.

2. Program description

2.1. Input

At the beginning of the program execution, the data are read in and stored for the subsequent refinement process. The user may choose to modify the parameters and redo the refinement with the same data.

The input information can be separated into three domains: (i) crystal information, (ii) measured data and (iii) refinement parameters.

(i) Crystal information: orientation matrix of the main reflections and the number of modulation vectors with rough estimates of their components ($\alpha_1, \beta_1, \gamma_1$) for \mathbf{q}_1 , ($\alpha_2, \beta_2, \gamma_2$) for \mathbf{q}_2 and ($\alpha_3, \beta_3, \gamma_3$) for \mathbf{q}_3 , respectively.

(ii) Measured data: the xyz peak positions in reciprocal space, the applied wavelength and the maximum order of observed satellite reflections. *NADA* uses the xyz peak positions with respect to a radius of the Ewald sphere $r_{\text{Ew}} = 1$. If the xyz peak positions are given with respect to $r_{\text{Ew}} = 1/\lambda$, the program will recompute them accordingly.

(iii) Refinement parameters: integer criterion used for re-indexing the peaks. Here the user has to specify the round-off error in order to accept a floating point number as an integer.

Data formats: for the input of the xyz peak positions, the wavelength and the orientation matrix, *NADA* currently supports the Oxford *CrysAlis* file format (Oxford, 2000) with *name.tab* (xyz peak positions) and *name.par* (orientation matrix and wavelength), the Stoe IPDS file format (Stoe, 1997) with *name.xyz* (xyz peak posi-

tions and wavelength) and *name.oma* (orientation matrix) and a *NADA* file format with *name.pli* (*xyz* peak positions) and *name.par* (orientation matrix and wavelength). All these files are ASCII files. The formats of the two *NADA* files are explained in detail in the online documentation (see below) and can be created with a standard text editor. Facilities for the input of the Bruker AXS SMART file format (Bruker, 1998) are in preparation.

The number of modulation vectors with the rough estimation of their components, the maximum order of the observed satellite reflections and the integer criterion have to be specified interactively by the user during the program execution.

2.2. Re-indexation

After successful reading, *NADA* first calculates the real *HKL* of all reflections from the orientation matrix **U** and the *xyz* peak positions (Giacovazzo *et al.*, 1992):

$$\begin{pmatrix} H_{i,\text{real}} \\ K_{i,\text{real}} \\ L_{i,\text{real}} \end{pmatrix} = \mathbf{U}^T \begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix}. \quad (4)$$

Using the maximum satellite order and the integer criterion, the peaks are re-indexed to integer *hklm*₁ (or *hklm*_{1m}₂ or *hklm*_{1m}_{2m}₃, respectively) by a trial-and-error method (one has to solve three equations with four, five and six unknowns, respectively).

$$\begin{aligned} h_i &= H_{i,\text{real}} - m_{1,i}\alpha_1 - m_{2,i}\alpha_2 - m_{3,i}\alpha_3, \\ k_i &= K_{i,\text{real}} - m_{1,i}\beta_1 - m_{2,i}\beta_2 - m_{3,i}\beta_3, \\ l_i &= L_{i,\text{real}} - m_{1,i}\gamma_1 - m_{2,i}\gamma_2 - m_{3,i}\gamma_3, \\ &\text{for } m_{1,i}, m_{2,i}, m_{3,i} = 0, \pm 1, \pm 2, \pm 3, \dots \end{aligned} \quad (5)$$

In this process, the *h*_{*i*}, *k*_{*i*}, *l*_{*i*}, *m*_{*1,i*}, *m*_{*2,i*} and *m*_{*3,i*} have to be integers. If a peak cannot be indexed successfully, it will be flagged and neglected during the refinement process.

2.3. Refinement

The refinement is performed by the method of least squares. The *xyz* peak positions are the observed data, whereas the indices *hklm*₁, *hklm*_{1m}₂ or *hklm*_{1m}_{2m}₃, respectively, are the control variables. Their relation is given by the orientation matrix and the modulation vector(s):

$$\begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix} = \mathbf{U}^T \begin{pmatrix} h_i \\ k_i \\ l_i \end{pmatrix} + \begin{pmatrix} \Delta x_{11} \\ \Delta x_{12} \\ \Delta x_{13} \end{pmatrix} m_{1,i} + \begin{pmatrix} \Delta x_{21} \\ \Delta x_{22} \\ \Delta x_{23} \end{pmatrix} m_{2,i} + \begin{pmatrix} \Delta x_{31} \\ \Delta x_{32} \\ \Delta x_{33} \end{pmatrix} m_{3,i}. \quad (6)$$

The Δx_{ij} are the components of the modulation vector(s) in the diffraction orthonormal coordinate system. After each refinement cycle, the sum of squared residuals is compared with the previous one. If the difference is smaller than 10^{-8} , the refinement is stopped. Stout & Jensen (1989) and Prince (1994) give a short introduction into the mathematics of least-squares refinement and calculation of standard uncertainties.

Typical running times depend strongly on the number of reflections and on the quality of the data, *i.e.* the number of refinement cycles, and last from a few seconds to less than a minute.

2.4. Output

The output information consists of the refined orientation matrix components with the derived cell parameters and the refined modulation vector(s) components. All values are given with standard

uncertainties calculated analytically by the Gaussian method of error propagation.

NADA produces three summary files (ASCII format): *name.s21*, *name.s22* and *name.s23*. In *name.s21* ('NadaSummary'), the final results of refinement [initial orientation matrix and modulation vector(s), wavelength, total number of peaks, maximum satellite order, integer criterion, number of cycles, number of indexed peaks, refined orientation matrix and modulation vector(s), lattice parameters] are given. In *name.s22* ('CycleSummary') the refinement process after each cycle is indicated (cycle number, total number of peaks, maximum satellite order, integer criterion, sum of squared residuals, degrees of freedom, estimated overall variance, number of indexed main and satellite reflections). In *name.s23* ('PeakSummary') all peaks are listed with their *xyz* positions, real *HKL* and integer *hklm*₁, *hklm*_{1m}₂ or *hklm*_{1m}_{2m}₃, respectively.

3. System requirements

3.1. Software

NADA was programmed in standard ANSI C in a Unix environment on a Silicon Graphics workstation. The World Wide Web interface is written in HTML and Perl. Only standard library functions are used. No overlay structure has been applied.

3.2. Hardware

The program should run on any computer with a Unix operating system (it has successfully compiled and executed on a Silicon Graphics workstation and on a Digital Alpha station). In addition, the program can be used *via* the Internet from a Web browser on any computer (Windows, Macintosh, Unix, ...) without any local installation. The interface has been successfully tested on different computer platforms from several worldwide locations using recent versions of Netscape Communicator and Microsoft Internet Explorer.

3.3. Availability

NADA belongs to the IC software projects of the Institute of Crystallography at the University of Lausanne. It can be executed from any computer with a recent Web browser *via* http://www-sphys.unil.ch/ic/SoftPro/nada_aa.html. It is also available as a free plugin for the Oxford *CrysAlis* software system (Oxford, 2000). *NADA* is free of charge to both academic and non-academic users.

3.4. Documentation

Online documentation with an explanation of program execution, a detailed description of the input and output data and a declaration of the refinement method is available at <http://www-sphys.unil.ch/ic/SoftPro/nada.html>.

4. Application and results

The authors and other users have satisfactorily tested the program with experimental data from the following compounds: (i) quininium (*R*)-mandelate, C₂₀H₂₅N₂O₅⁺·C₈H₇O₃⁻, with one-dimensional incommensurate modulation [Stoe IPDS, Mo *K* α and Oxford Xcalibur CCD system, Mo *K* α and MAR IP, synchrotron (the MAR IP data have been analysed with the Oxford *CrysAlis* software system)]; (ii) sodium carbonate, γ -Na₂CO₃, with one-dimensional incommensurate modulation (Oxford Xcalibur CCD system, Mo *K* α); (iii) melilite, Ca₂MgSi₂O₇, with two-dimensional incommensurate modulation

Table 1

Comparison of lattice parameters refined with main reflections only and refined with main and satellite reflections.

In the latter case, the modulation vector(s) components are also given.

	Main reflections only	Main reflections and satellites
Quininium (<i>R</i>)-mandelate		
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.603 (11), 18.612 (26), 10.408 (17)	6.602 (4), 18.615 (11), 10.406 (7)
α , β , γ (°)	89.99 (13), 107.53 (10), 89.93 (17)	90.00 (5), 107.53 (4), 89.93 (7)
\mathbf{q}_1 (α_1 , β_1 , γ_1)	–	0.3339 (4), –0.0041 (9), –0.2737 (5)
Melilite		
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.834 (2), 7.845 (2), 5.015 (2)	7.839 (1), 7.845 (1), 5.015 (1)
α , β , γ (°)	90.00 (3), 90.00 (1), 90.01 (2)	90.00 (2), 90.00 (1), 90.01 (1)
\mathbf{q}_1 (α_1 , β_1 , γ_1)	–	0.2810 (3), 0.2814 (4), –0.0001 (2)
\mathbf{q}_2 (α_2 , β_2 , γ_2)	–	–0.2812 (3), 0.2815 (4), 0.0000 (3)

(Oxford Xcalibur CCD system, MoK α); (iv) pyrophosphate, ZrP₂O₇, with three-dimensional commensurate modulation [MAR IP, synchrotron (the MAR IP data have been analysed with Oxford CrysAlis software system)].

In Table 1, the lattice parameters of quininium (*R*)-mandelate (Stoe IPDS) and those of Melilite (Oxford Xcalibur CCD system) are shown, calculated in one case with main reflections only and in the other case using main and satellite reflections.

In addition, *NADA* can also be used as a fast and easy tool to detect the commensurate or incommensurate character of the sample and thus to obtain information for the further modelling of the crystal.

5. Notes for program users

In order to derive good estimates of the orientation matrix and modulation vector components, the starting values for the modula-

tion vector(s) components should be as accurate as possible. These numbers can be obtained for example by careful analysis of the real *HKL* of the peaks. It is also important to consider the systematic absences (the shortest possible vector is not always the right one).

It is also good practice to start the refinement with only low-order satellites and a small integer criterion for *hklm*₁, *hklm*_{1m}₂ or *hklm*_{1m}_{2m}₃, respectively. Later these values can be increased step by step, after successful refinement.

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