Jana2000

Crystallographic computing system

Václav Petříček & Michal Dušek
Institute of Physics
Academy of Science of the Czech Republic

User manual, part 1

Edited by Michal Dušek, Václav Petříček, Karla Fejfarová & Lukáš Palatinus
Praha 2003

Contents

Preface

Jana2000 is a system for solving and refinement of regular, modulated and composite structures from both single crystal diffraction data and powders. It is compatible with previous version JANA98 but its functionality is extended.

Jana2000 covers the basic tasks of structure analysis from data reduction and powder profile analysis to the solution of the phase problem, structure refinement and presentation of results. The three-dimensional and higher-dimensional crystals are treated uniquely in one system regardless of the data type (single crystal or powder). In addition to regular structure parameters and their modulation (occupancy, atomic position and harmonic ADP) the system can also be used for refinement of anharmonic ADP, multipole refinement and f', f'' refinement. Multiphase refinement is available for both powder and single crystal data.

This manual consists of three basic parts: The first part (*Basic concepts*) introduces Jana2000 with help of several solved examples. In the second part (*Parameters*) all structure and profile parameters used in the program are defined. It also explains the format of parameter files M40 and M41 and the ways to edit these files. The third part (*Structure analysis*) describes the whole process from input of data and solution of the phase problem to structure refinement and interpretation of results. It describes the basic programs of Jana2000. The last part (*Special topics*) contains comprehensive chapter about transformations and several case studies about work with twins, five-dimensional structures, overlapped reflections, multipole refinement etc.

We hope the book will be useful for both beginners and advanced users and we welcome any reader's comment.

Václav Petříček
Michal Dušek

1
Basic concepts

This part of the manual is intended as an introduction to Jana2000. It is focused to practical skills and it skips details and theory. The other chapters will describe Jana2000 in a more systematic way and they will require some preliminary experience with the program.

Introduction describes briefly installation, customization, execution and organization of the program. The details about installation and customization that are not so frequently needed are described in Appendices. In *Introduction* we shall also learn about communication of the principle tools of Jana2000 through the basic files, about naming conventions of atoms etc. Finally, a complete map of Jana2000 tools is shown with links to related sections of the manual.

In the next part, we present five solved examples: *Standard structure from single crystal*, *Standard structure from powder*, *Modulated structure from single crystal*, *Modulated structure from single crystal* and *Advanced powder refinement*. We describe the complete structure analysis in each example with special emphasis to utilization of the program tools. The examples are available in the internet.

After reading *Basic concepts,* the reader should be able to use Jana2000 for normal work.

1.1 Introduction

1.1.1 Installation

Jana2000 is freely available on the **Jana2000 homepage**[1] or on the **anonymous ftp**[2] server. The following files can be downloaded:

README.TXT	Downloading and installation notes
jana2000Pack.exe	The self extracting installation file for UNIX
jana2000.tar.gz	Installation files for UNIX compressed by gzip
janainst.exe	Files for Windows containing the executable optimized for Intel Pentium Pro, Pentium II, Pentium III and compatible processors.[3]
manual2000.pdf **manual2000.doc**	this manual

The recommended way of installation for UNIX is processing of jana2000Pack.exe[4] by command

```
source jana2000Pack.exe
```

executed from the prompt of *csh* or *tcsh*.
For Windows the installation is started by executing janainst.exe.
In both cases, the installation is self-explanatory. Details are given in Appendix A.

1.1.2 Executing Jana2000

The program can be started from the command line, by an icon or through an associated file type. More sessions of *Jana2000* can run together, even in the same directory, assuming that they are using different job names.

1.1.2.1 Command line syntax

Version for Windows

```
jana2000 [jobname] [@filename]
```

Version for UNIX

```
jana2000 [jobname] [options] [@filename] [&]
```

Symbol	Meaning
jobname	base name of all permanent files of the structure
@filename	Starts *Jana2000* in a batch mode without graphical interface using commands from *filename*. This option is under development. Please contact authors if you want to use it.

[1] http://www-xray.fzu.cz/jana/jana.html
[2] ftp://ftp.fzu.cz/pub/cryst
[3] Versions for older processors, for instance 486, will be delivered upon request.
[4] The extension *exe* is used in order to convince Web browsers that it is a binary file. In fact the file is not executable. It is combination of an ASCII header and a binary archive.

Options (only for UNIX version)	
-geometry *wxh±x±y*	Sets window geometry according to conventions for X11 graphics[1]. Better way of controlling window size is through Preferences (see later). Example: `jana2000 my_structure -geometry 500x400+100-50` *Jana2000* will automatically fix the ratio between width and height as it is fixed in the program. It will also change too small or too large window dimensions.
-scale *number*	Sets height of the window as % of the display height.
-iconic	Starts *Jana2000* minimized.
-skipini	Skips reading of initialisation file.
-dir *dirname*	Sets working directory. Normally *JANA2000* starts in the last used directory.
-help	Lists command line syntax.
&	(at the end of the command) The program will start in the background

1.1.2.2 File names

Jobname determines the file names belonging to the calculated structure. They differ by an extension of three characters, for instance *jobname*.m50. This convention is also used in the UNIX version.

Case sensitivity

The file names under Windows are case insensitive, i.e. *jobname*.m50 is the same as *JobName*.M50. Under UNIX, the file names are case sensitive. Thus, we can work with two different structures *jobname* and *Jobname*. The filename extensions must be always in the lowercase. For instance, the file *jobname*.M50 will not be recognized by UNIX version of *Jana2000*.

Basic files

The basic files are M50, M40, M95, M94, M91 and SMR for single crystals, M50, M41, M40, M92 and SMR for powders. They are summarized in the following table.

Basic file	Description
Jobname.m50	Basic crystal information, options for programs
Jobname.m40	Parameters of structure model
Jobname.m41	Profile parameters (powders)
Jobname.m95	Diffractometer file (single crystals)
Jobname.m94	Header of M95
Jobname.m92	Profile data (powders)
Jobname.m91	Reflections for refinement (single crystals)
Jobname.smr	Information for creating CIF file

[1] The coordinates following the "-geometry"-option determine the size (in pixels) of the application window and its position, <x-size>x<y-size><sign><x-position><sign><y-position>. The positions are relative to the left or upper edges of the screen if <sign> is positive, to the right or lower edges if <sign> is negative.

End-of-line conversion

The ASCII files use special non-printable characters to indicate end of lines. In Windows it is the ASCII code 10 (LF[1]) followed by 13 (CR), in UNIX it is the ASCII code 10 (LF). *Jana2000* automatically converts the ends of lines between UNIX and Windows in the basic files and in most of other imported files[2].

Listing files

Name	Description
Jobname.ref	Listing of Refine
Jobname.fou	Listing of Fourier
Jobname.rre	Listing of data processing and averaging
Jobname.dis	Listing of Dist

Temporary files

Jana2000 creates two kinds of temporary files.

- Files *jobname*.lnn, where *lnn* is an extension composed of character *l* and two digits, are stored in the current directory. During the regular end[3] of *Jana2000* they are automatically deleted.
- Files jcmd*, jm* and *.pcx are saved in the temporary directory. For Windows version it is *JANADIR*\TMP, for UNIX it is one of /scratch, /var/tmp, /tmp or *$(HOME*). The temporary directory can be redefined by *Tools* → *Preferences*. *Jana2000* deletes the temporary files during the regular end. It also scans the temporary directory for temporary files from improperly terminated runs and if their number exceeds some limit, it offers their deleting.

Complete overview of files in Jana2000 is in Appendix D.

1.1.3 User preferences

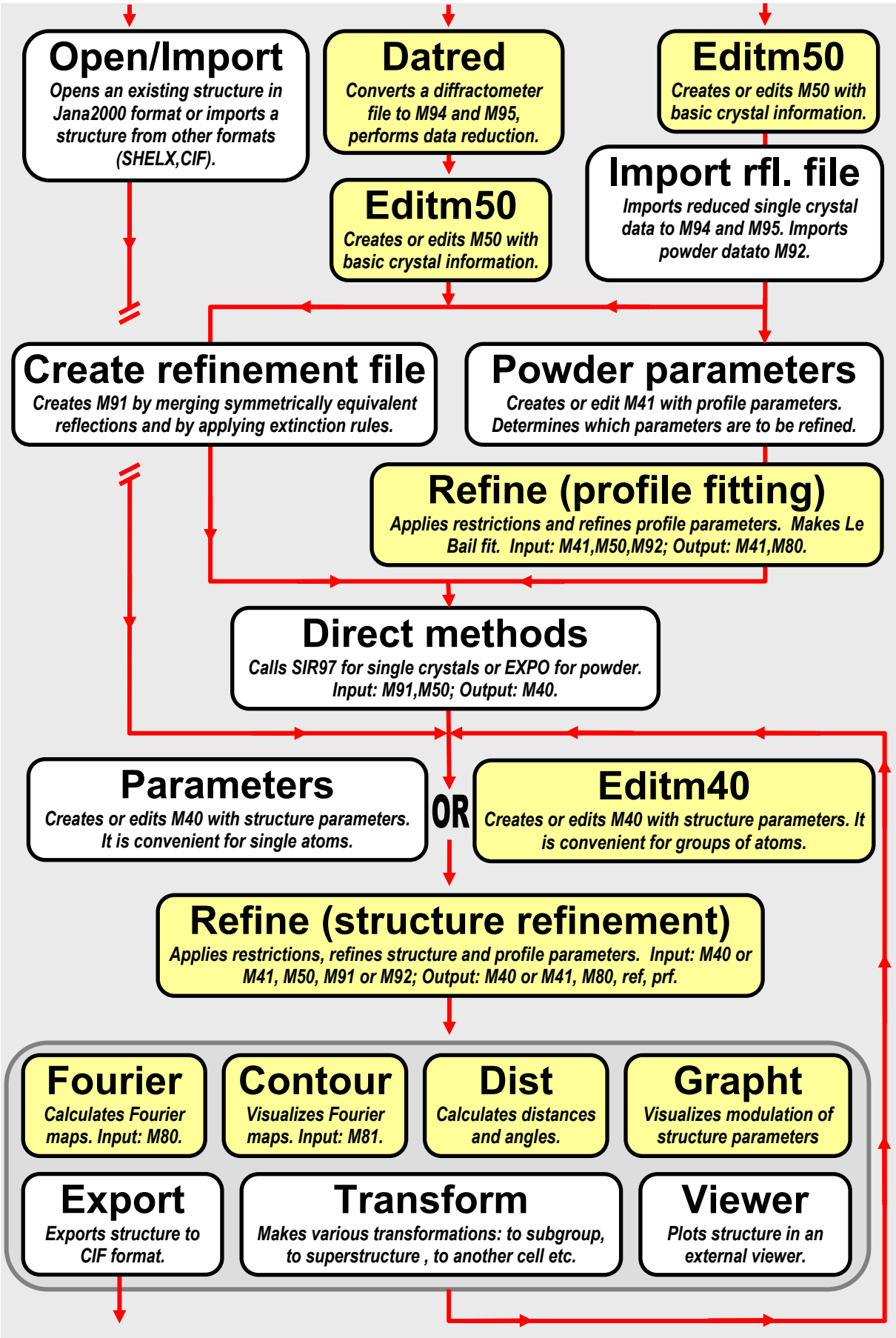
User preferences are set through *Tools* → *Preferences* and they are saved to jana2000.ini. For both versions, they can be used to set size and position of the *Jana2000* window, path to temporary space and external programs. Details are given in Appendix B.

[1] LF is Line Feed; CR is Carriage Return.

[2] Diffractometer files, SHELX files etc.

[3] The Regular end occurs when the program is quitted by File → exit. For Windows the Regular end occurs also when the window is closed by the cross in the title bar. Under UNIX, this is not considered a Regular end because of difficulties with testing of Destroy event within the program.

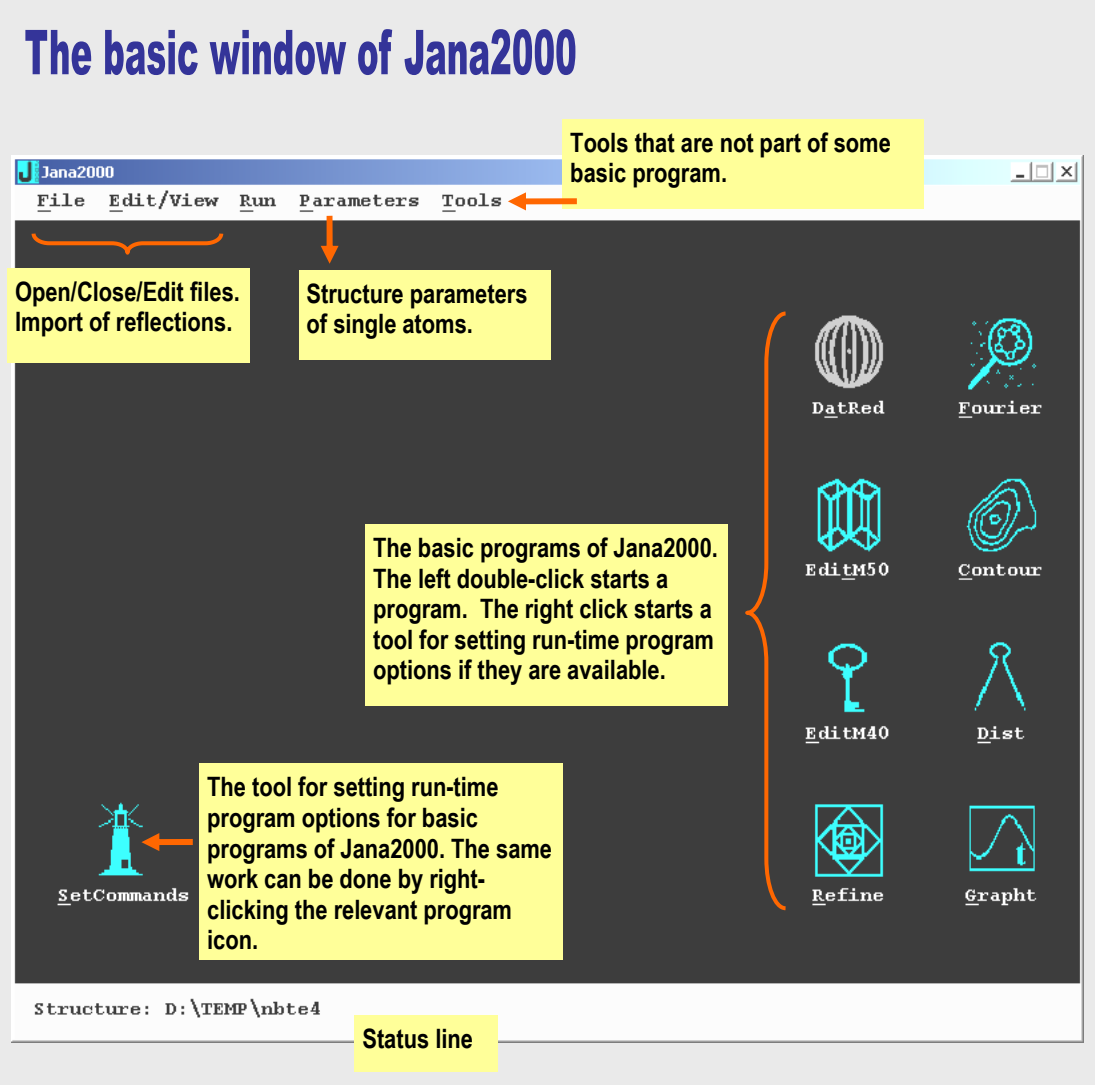
1.1.4 Flowchart of Jana2000



The yellow boxes indicate tools that are started through an icon in the basic window of Jana2000. The tools shown in the white boxes are started through a menu. Only the most important input and output files are shown.

1.1.5 Basic window of Jana2000

Programs of *Jana2000* can be executed through their icons in the program basic window or through the menu *Run*. The menu *Tools* lists items that are not classifiable as a part of some basic program. The menu *Parameters* can be used for viewing or setting structure parameters of single atoms. The work with the program starts either with *Datred* icon (reading of a diffractometer file) or with *File* menu (opening of an existing structure, import of a reduced reflection file).



1.1.6 Graphical interface

The graphic user interface supports an intuitive way of work. Its behavior is the same in UNIX and Windows because the graphical objects are programmed specially for *Jana2000*. This makes the program independent of the environment but, on the other hand, some differences from commonly used conventions occur in *Jana2000*.

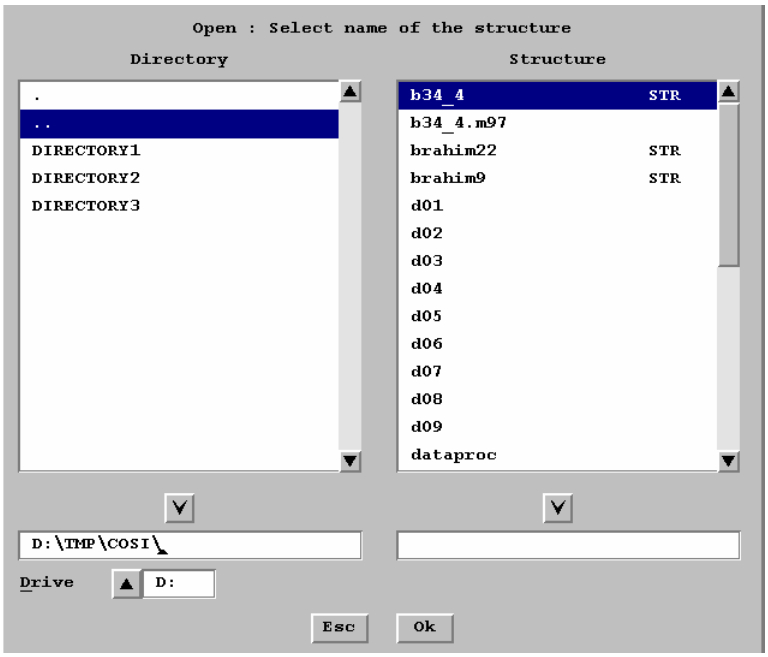
- TAB changes focus between text boxes. In many cases, it also starts processing of changes made in the textbox that is just left. For instance, in *EditM50*, we can change the space group symbol. After pressing TAB the new symmetry operators will appear in the relevant text boxes. With new structure, we can also increase (with help of *EditM50*) number of dimensions. After pressing TAB new text boxes appear for definition of q-vector.
- Ctrl-Y clears the text box under the cursor.
- ENTER selects button OK. Pressing ENTER twice is equivalent to clicking OK by mouse.
- No cut-and paste operations are available.
- No context menus started by the right mouse button.
- No sub-windows. Any new "window" is plotted in the basic window and cannot be moved by mouse.
- The basic window of *Jana2000* can be resized by mouse only in the basic state, i.e. when no program is running.
- Ctrl-letter starts programs. For instance, Ctrl-A starts *Datred*.
- Alt-letter opens menu. For instance, Alt-T open *Tools*. In a user forms (for instance *Symmetry* in *EditM50*) Alt-letter selects an item in the form.
- Letter selects item in a menu. For instance, Alt-T followed by g starts *Graphic viewer*.
- In UNIX version, the Close button of the window manager is ignored by Jana2000. The Destroy button closes the window but leaves the temporary files undeleted. For this reason, the UNIX version should be always closed by *File* → *Exit* or by quickly pressing Ctrl-X four times. In Windows, this problem does not exist.

File manager

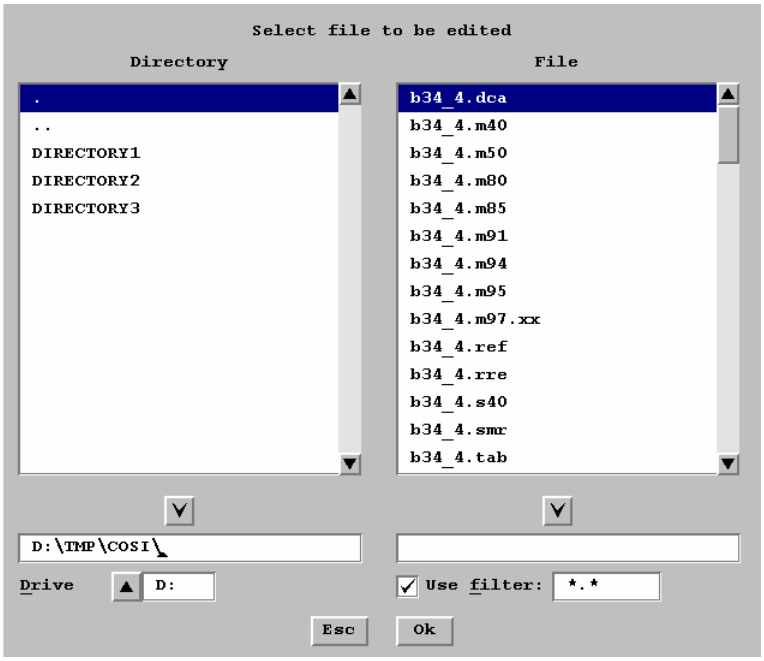
The *File manager* of *Jana2000* is used for selection of structures or files. In the mode for selecting structures, it detects Jana files and shows only one name per structure with a flag STR. For data files, it adds a flag DAT, the remaining files are listed one-by-one without flags. In the mode for selecting files it lists all files that correspond to *Filter*.

In the left panel, double-click on a directory name or *".."* changes the directory. The current version does not support creation of a new directory. In the right panel, the check button as well as double-click copies the selected file name or a structure to the text box. *OK* with a string in the textbox starts the action. If the structure or filename written in the textbox do not exist they are created - this is especially used for opening a new structure.

File manager in the mode for selecting structures



File manager in the mode for selecting files



1.1.7 Atom naming conventions

Each atom of the structure model has a name listed in the refinement parameter file M40. The length of the name is limited to eight characters, but ***the recommended length is 5 characters*** as in some cases *Jana2000* appends another characters to the end of the atom name. The names are ***case insensitive***.

Wildcards

In *restric*, *equation* and *fixed* commands of *Refine* and the *center* command of *Fourier* groups of atoms can be defined using the wildcards. The wildcards have the usual meaning:

*Sn** denotes all names starting with string "sn" (case insensitive).
S? denotes all names starting with "s" and containing two characters .
*?a** denotes names having the letter "a" in the second position.

Molecular positions

If an atom is a part of a molecule, a character denoting the molecular position is appended to the name. For instance, atom As of a model molecule has name Asa in the 1st position, Asb in the 2nd one etc.

These extended names can be used for definition of a general plane, in the *select* command of *Dist* etc. They cannot be used in the refinement restriction commands because they are not explicitly present in the M40 file.

The internal symmetry codes

Some tools of *Jana2000* accept the internal symmetry codes indicating symmetry position of the atom. An internal symmetry code follows immediately the name of an atom in M40. It takes a symbolic form `#sncmtijk` , where

`#` separates the internal symmetry code from the atom name.
`sn` specifies the $|n|^{th}$ symmetry operator from M50 file. If n is negative, the operation is combined with the center of symmetry[1].
`cm` specifies that the m^{th} centering vector will be added to the result of the symmetry transformation s_n (The centering vectors are listed in the basic crystal information part of any *Jana2000* listing)
`tijk` specifies the additional cell translation defined by three integers *i,j,k*.

Examples:

```
Si3#s-3c2t1,-1,0
```

(Position of Si3 in M40 transformed by the 3rd symmetry operator, by the center of symmetry, by the 2nd centering vector and by the translation 1,-1,0)

```
Na1#s2
Cr4#t1,0,-1
```

An atom name together with an internal symmetry code can exceed the length of 8 characters because it is never present in the m40 file. The internal symmetry codes can be used in *Contour* for the definition of the general section plane and in *Grapht* for plotting *t* functions. They are listed in the one-column form[2] of the listing of *Dist* or by *Locator* tool of *Grapht*.

[1] if it exists in the structure - otherwise an error message occurs
[2] It can be selected in the basic commands for Dist.

1.1.8 Basic steps with Jana2000

In this part we shall describe the basic steps with *Jana2000* during typical structure analysis. It is based on the *Flowchart of Jana2000* (§ 1.1.4) and on the brief description of *Jana* files in § 1.1.2.2 .

Input of data

At the beginning, we need to read diffraction data and input the basic crystallographic information. *Jana2000* offers three ways how to begin.

- ***Open/Import*** (started from the menu *File* → *Structure* → *Open* or *File* → *Import*) works with a previously defined structure.
- ***Datred*** starts from a diffractometer file, performs data reduction and converts the file to M94 and M95 (the common diffractometer format). Then the basic crystal information must be defined by *EditM50* that yields the file M50.
- The last possibility (*File* → *Reflection file* → *Import*) is used (1) if no diffractometer file is available, (2) for powder data and (3) for joining data from various sources.[1] The imported reflections must be already reduced by other software or by *Datred*. This tool is very flexible; it enables transformations between cells and dimensions and it is explained later in this manual. Like in the previous example, the imported reflections are converted to the M94 and M95 format.

Determination of symmetry

Jana2000 offers only limited tools for finding proper symmetry. In *Datred* there is possibility to calculate the *Point group test* that reads reflections from M95 and lists R_{int} for a given point group symmetry. The systematic absences are listed during creation of the refinement file M91 (*File* → *Reflection file* → *Create refinement file*) after entering the tentative (super)space group in *EditM50*.

Solution of the phase problem

No tools are available for automatic structure determination. However, *Jana2000* can exchange information with SIR97 [1] and EXPO [2] that solve structures by direct methods. For calling these programs from *Jana2000* M50 and M91 files are necessary. The file M91 contains non-extinct reflections merged by symmetry. The resulting structure model from direct methods is imported to the file M40.

Another way to solve the phase problem is the classical (non-automatic) heavy atom method. For calculating Paterson map we need file M80 that is created by program *Refine*. Because no structure is available in this stage, we need only M50 and M91 for *Refine* and we run only zero refinement cycles[2]. Then we run *Fourier* and read the positions of the Patterson peaks in the Fourier listing[3]. The position of the heavy atom can be inserted to M40 by *EditM40*.

Powder profile refinement

In case of powder data, M91 is created by decomposition of the powder profile. Therefore, the profile refinement must precede the solution of the phase problem. The menu *Parameters* → *Powder* is used for selection of profile parameters and their

[1] Typically, twin domains are measured or integrated independently and the data must be joined.

[2] The options for Refine and Fourier are activated by clicking the relevant icon by the right mouse button.

[3] The listing viewer is started through Edit/View menu.

refinement keys. *Refine* makes the profile refinement and LeBail decomposition. The powder profile can be studied with the *Profile viewer* (menu *Tools* → *Powder*).

Structure refinement

For refinement, we need files M40, M50 and M91. M40 contains parameters of the structure model and refinement keys. With default setting all parameters are refined that are not restricted by the symmetry with exception of scale parameters, site occupation and twin volumes that are implicitly fixed.
Refine has many refinement options accessible by clicking the right mouse button. The results of the refinement are summarized in the screen and the details are printed to the refinement listing. Before another refinement we usually need to edit the structure model. This can be done by program *EditM40* that supports editing of parameters for groups of atoms. A tool started through menu *Parameters* supports single atom editing.

For powder data, *Refine* makes Rietveld refinement. The refinement of profile parameters can be controlled by menu *Tools* → *Powder*. In case of more powder phases another phase is added by *Tools* → *Phases*. An important limitation exists in Jana2000: the structure of the new phase must be known and added in M40 by *EditM40*. In other words, combination of the profile refinement and Rietveld refinement is not possible.

Fourier maps

Fourier maps are calculated by *Fourier* that reads M80 as an input. The file M80 contains Fourier coefficients and it is prepared by *Refine* after the last refinement cycle. With Fourier options, a variety of maps can be calculated. *Contour* is used for visualization of two-dimensional sections through Fourier maps. *EditM40* can be used for adding Fourier maxima to M40.

Dist, Grapht, external viewer

Dist calculates distances, best planes and torsion angles. For modulated structures, the distances are calculated in steps of the internal coordinate *t*. *Grapht* is activated only for modulated structures. It plots various structure parameters as a function of the internal coordinate *t*. An external viewer is started by *Tools* → *Graphic viewer*. It can be any plotting program that accepts CIF file as a command line argument. Very well tested is communication with program Diamond [3].

How to activate Powder option

With powder structure, we first define the basic crystal information in *EditM50*. Then the import of the powder experimental profile is possible by *File* → *Reflection file* → *Import.* As soon as we choose to import powder data, the powder option of *Jana2000* is activated and fixed. The graphic interface does not allow change of a powder structure back to a single crystal structure and *vice versa*.

How to activate modulated structure

Modulated structure is activated by setting number of dimensions in the *Cell* subwindow of *EditM50*. Then we can import reflections by *File* → *Reflection file* → *Import.* After the import of reflections the possibility to change number of dimensions is disabled. It is activated again if we delete M94 and M95.

Another way is to import a diffractometer file by *Datred*. Before the import number of dimensions must be set and for some diffractometers also **q** vector(s) must be defined. Some diffractometers allow measurement of satellite reflections with three real indices. In these cases *Datred* converts automatically to 4 or more indices.

Transformations

The menu *Tools* → *Transformations* offers several types of transformations that will be discussed later in detail. The simplest case is the cell transformation. The transformations change M50, M40 and M91. In M94, the transformation matrix is saved so that M95 is still consistent with the transformed structure. For instance, creation of the refinement reflection file can be repeated even with the transformed structure despite the fact M95 is unchanged.

If we change symmetry by *EditM50*, i.e. without using a transformation tool, the relevant changes of the structure model and preparation of the refinement reflection file must be done by the user. *EditM40* contains tools for transformation or expansion of the structure model by symmetry operators or by user-defined matrices.

Absorption correction

Absorption correction is calculated by *Datred*. The correction factors are saved in M95 and they are applied when the refinement reflection file M91 is created. Therefore, the absorption can be repeated or removed. This is useful when the chemical composition is not completely known at the beginning of the structure analysis. Absorption correction can be calculated only if M95 has been created from a diffractometer file by *Datred*. M95 created by Import does not contain direction cosines.

Work with twins

The *Cell* subwindow of *EditM50* can be used for setting the number of twin domains and for definition of the corresponding twin matrices. In the menu *Parameters* → *Scale*/*Twin,* we can then define volumes of the twin domains and their refinement keys. If the twinning matrices are composed only of integers, the reflections of twin domains are completely overlapped. *Refine* uses the twinning matrices to combine corresponding reflections during calculation of structure factors.

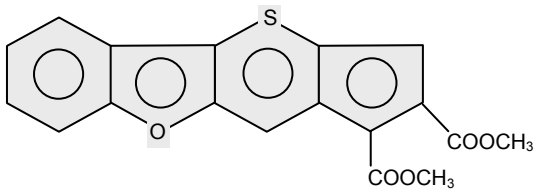
If reflections of the twin domains are only partially overlapped the twin domains should be measured or integrated independently using their local orientation matrices. Then we proceed this way:

- In *Jana2000* we open new structure *twin1* and read the diffractometer file of the first twin domain. We make data reduction and absorption correction, if applicable,
- We create *twin2* and do the same with data of the second twin domain. In case of more domains we prepare *twin3*, *twin4* etc. by the same procedure.
- Finally, we open new structure *twin*, define the basic crystal information in *EditM50* (including the number of twin domains and their twinning matrices) and import files M95 of *twin1*, *twin2*, *twin3* …. as the twin No 1,2,3 …

In the basic refinement option, a threshold can be defined to determine which reflections are overlapped and which are separated. A similar approach can be used for joining diffractometer files of the same crystal measured on more diffractometers.

1.2 Standard structure from single crystal

In this chapter, we present solution of a simple organic structure [4] with structural chemical formula



and with the basic crystallographic data summarized in this table:

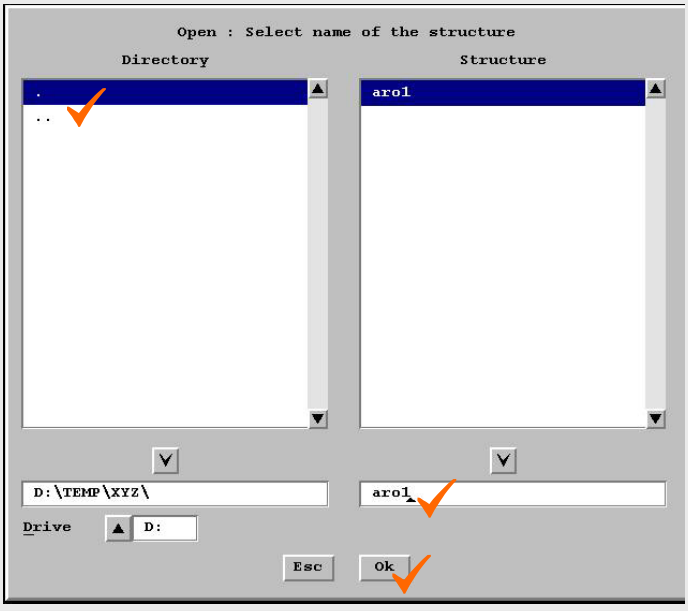
Cell parameters (a,b,c,β)	a=14.963Å, b= 5.083Å, c=20.099Å, β= 104.15°
Radiation:	MoKα
Monochromator angle	6.07°
Space group	$P2_1/n$
Chemical formula	$S_4O_{20}C_{72}H_{48}$

The crystal data measured with four-circle diffractometer are available in the Jana Web page as **aro1.zip**.[1] The archive contains a diffractometer input file aro1.dca.

1.2.1 Starting Jana2000

When executed without command line parameters, *Jana2000* starts automatically in the last used directory and with the last used job name printed in the status bar[2]. To open a new job *aro1* we have to do the following:

- (optional) Create a directory and copy aro1.dca here.
- Start *Jana2000*
- Start File manager of *Jana2000* by *File* → *Structure* → *Open*
- Use the left panel to skip to the proper directory
- Define the job name in the text box in the right panel
- Press OK



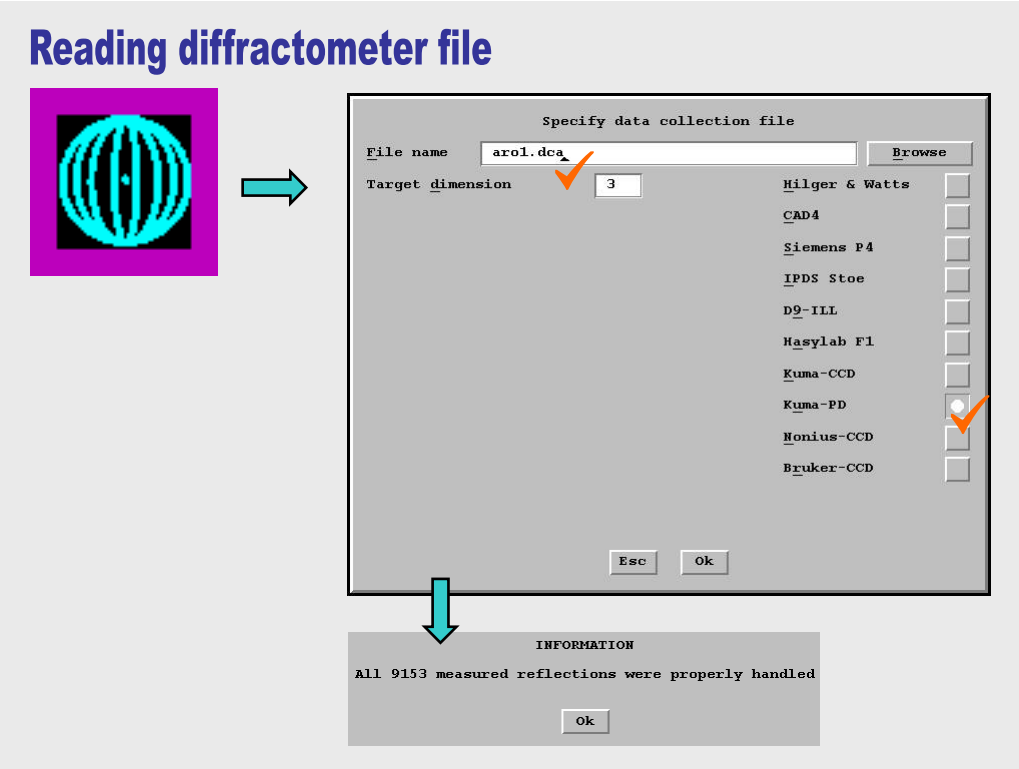
File Manager

[1] http://www-xray.fzu.cz/jana/Jana2000/manual/examples/aro1.zip

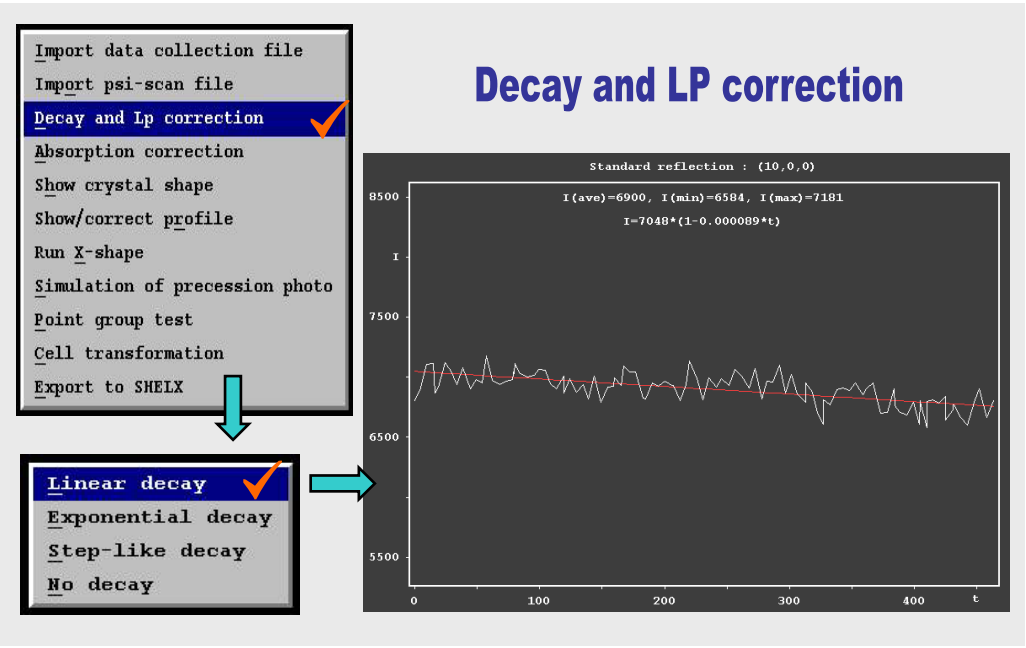
[2] At this stage, Jana2000 do not open or test any files of the job.

1.2.2 Input of data

At the first step, we start the program *Datred* in order to read the diffractometer file aro1.dca. As no M95 exists, *Datred* opens directly the form for input from diffractometer. We choose *Kuma PD*, which is the original name of the Xcalibur diffractometer, find aro1.dca and press OK. *Datred* will transfer reflections and the basic crystallographic information to M94 and M95.

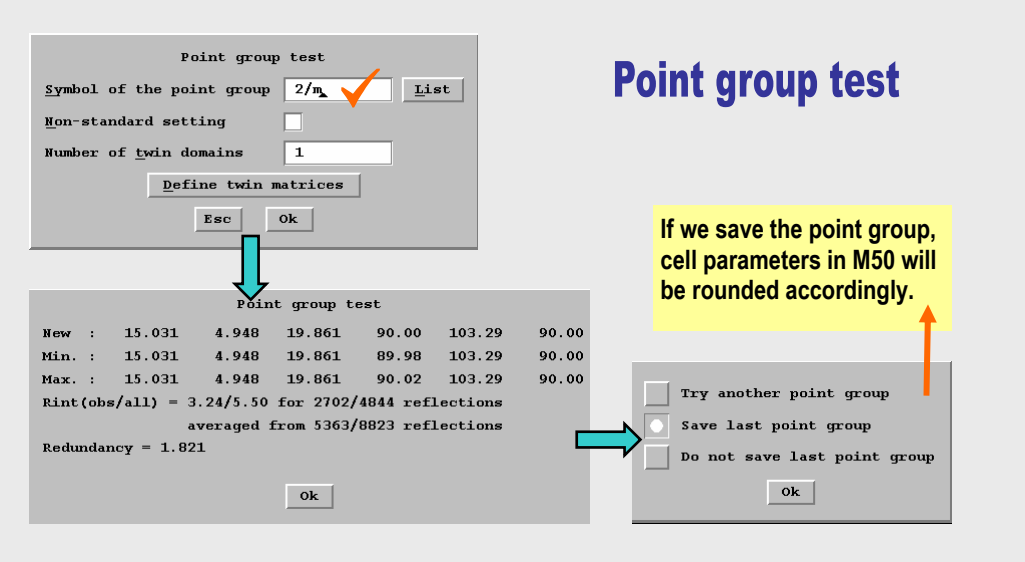


In the next step, we correct the data by *Decay and LP correction*. Absorption correction will be omitted since it is negligible for this crystal.



1.2.3 Determination of the space group, solution of the phase problem

The current version of *Datred* has no automatic tool for space group determination[1]. The *Point group test* lists R_{int} for a given point group. In our example the point group test for the point group 2/m indicates the monoclinic symmetry. The systematic extinctions can be tested visually in the *Reciprocal space viewer* (started from menu *Tools*). Another possibility is to define a tentative space grup in *EditM50*, create the refinement reflection file by *File* → *Reflection file* and view the list of discarded reflections in the *Reflection report* aro1.rre with help of the *Edit/View* menu.



1.2.4 Program Editm50

The program *EditM50* is used for entering or editing the basic crystallographic information. It is saved in the file M50[2].

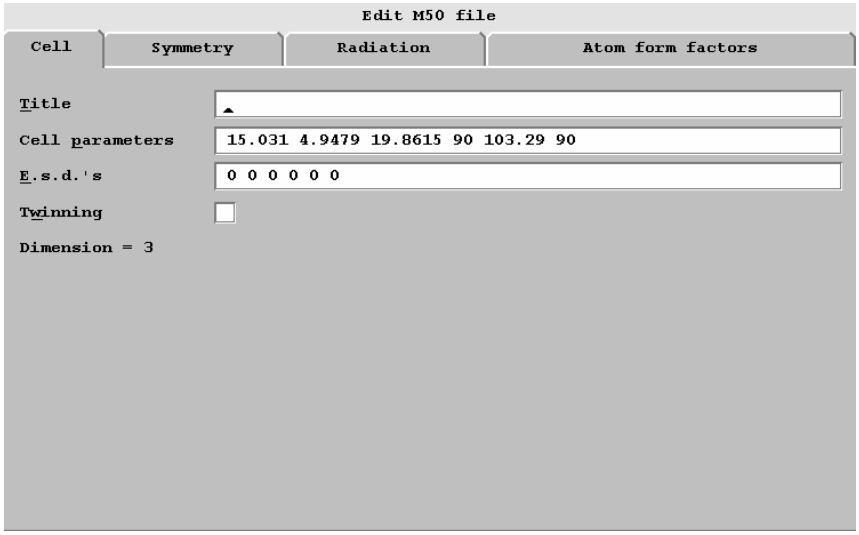
1.2.4.1 Cell parameters

When started from the diffractometer file the cell parameters are already preset in *EditM50*. If the results of the *Point group test* have been saved, they are already rounded according to the point symmetry; otherwise they must be rounded by the user to be consistent with the proposed space group. The *e.s.d* textbox can be left clear as the standard deviations of cell parameters are only used for the CIF output and they are not taken into account in calculation of s.u. of distances[3].

[1] This is for historical reasons as originally Jana was not intended for *ab initio* solutions. Various external programs, for instance XPREP, read hkl file in the SHELX format as input. This can be prepared by *Datred* → *Export to SHELX*.

[2] The file M94 contains the original cell parameters read from the diffractometer file. M50 contains the final cell parameters that are consistent with the structure model and the used symmetry.

[3] In future versions of Jana they will be taken into account.

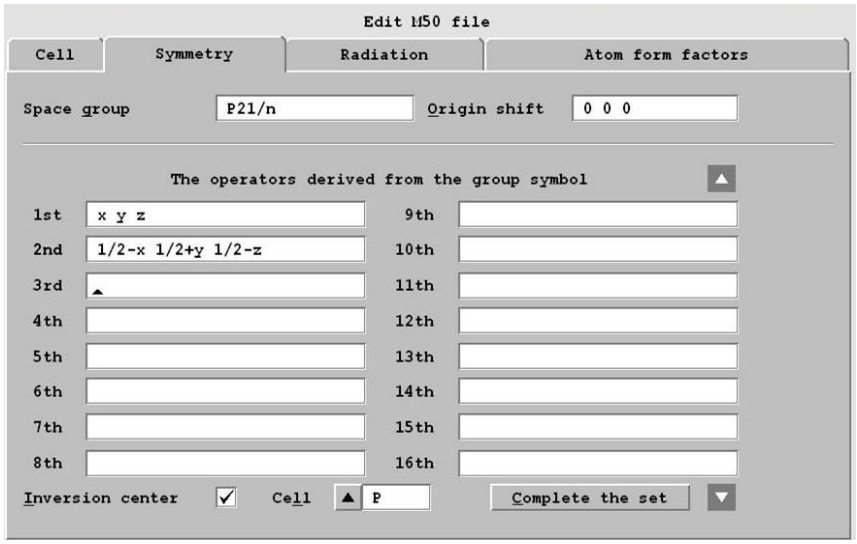


1.2.4.2 Symmetry

The *Symmetry form* is divided into two parts. The upper part contains the space group name and the origin shift with respect to the standard choice for the relevant space group. The lower part contains the symmetry operators, the indicator of the inversion center at the origin and the cell centering information. Note that in the case when the inversion center is present but not in the origin, the indicator cannot be used.

The upper part can be used to define the space group by its symbol and for the origin specification. The lower part is filled by the derived information whenever the upper information is filled.

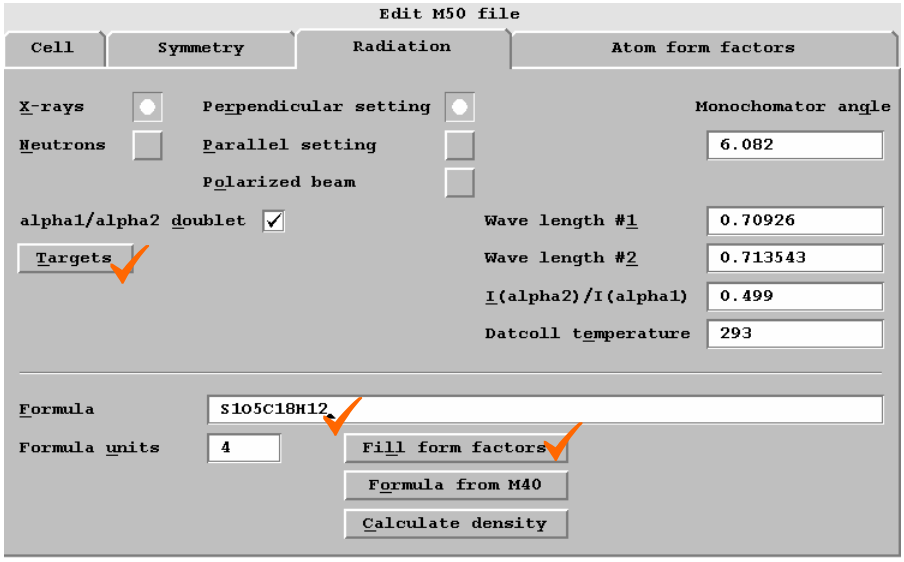
The lower part can be used to define the symmetry explicitly by the symmetry operators, the cell centering and the presence of the inversion center at the origin. Any subset of operators which already generates the proper space group is sufficient as the button *Complete the set* will generate the rest. Then the program will also try to derive the symbol and the origin shift with respect to the standard choice. The procedure for deriving of the space group symbol is successful only if the selection of the cell is in agreement with the basic rules. All permutations of the cell parameters are acceptable for triclinic, monoclinic and orthorhombic symmetries. The higher symmetries except the cubic one should have the dominant axis along c. Nevertheless all possible settings even those with cannot yield a conventional symbol are acceptable by the system.



1.2.4.3 Wavelength and atom form factors

In the *Radiation* subwindow, we can choose or modify the type of radiation and the wavelength[1]. In our example, the classical Mo radiation is used. The cathode material can be defined by the button *Targets*.

Formula defines chemical composition that is necessary for density calculation and absorption correction. If we have already done the absorption correction in *Datred* the formula field is prefilled. Numbers (including "1") must delimit the chemical elements, for instance Na2C1O3. The button *Fill form factors* can be used for definition of the atom form factors based on the formula. The coefficients are saved in M50 in the order given in the formula[2]; i.e. the first atom form factor in M50 corresponds to the first atom in the formula etc. Using of Fill form factors is not the only way to define atom form factors. They can be also defined independently of the formula using the last subwindow of Editm50.



1.2.5 Creating the refinement reflection file

After quitting Editm50, the program offers creation of the refinement reflection file M91[3]. M91 is created from M95 by applying the corrections defined in M95, by excluding the systematically extinct reflections and (optionally) by averaging the reflections according to the symmetry. The limit for observed reflections (see the flowchart) is only used for printing the import statistics and R_{int}. The chosen sigma (Poisson) results from the counting statistics.

The detailed information about systematic extinctions and averaging of reflections is available in the *Reflection report* (jobname.rre) accessible by the *Edit/View* menu. The information about *averaging* is important for estimation of data quality and for approving of the symmetry.

In the scheme below we can see the program discarded the strong reflection -4 0 5. The corresponding peak in the *Profile viewer*[4] of *Datred* is shifted from the centre so that it may be just a tail of some neighboring reflection.

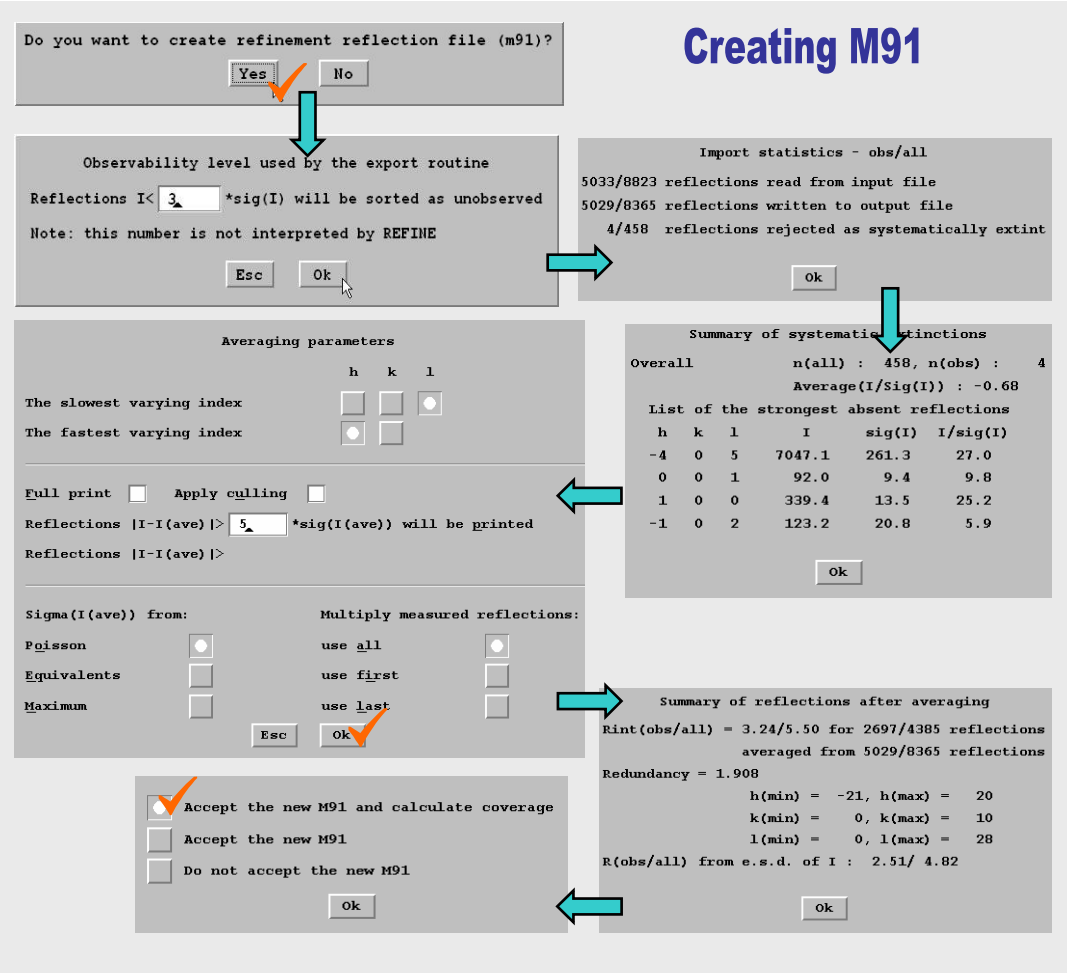
---

[1] The initial values are taken from the diffractometer file.

[2] In M40 file (structure parameters), the atom form factors are referenced to by their sequence number in M50. Therefore, the order of elements cannot be changed when a structure already exists in M40.

[3] It can be also created using the menu *File→ Reflection File*.

[4] The profile viewer is enabled because the input diffractometer file DCA contains diffraction profiles.



1.2.6 Solution of the phase problem

1.2.6.1 Solution with SIR97

SIR97 [1] can be called by *Jana2000* as an external program by *Run* → *Solution SIR97*. The program is available in **http://www.irmec.ba.cnr.it** for both Windows and Unix. The path to *SIR97* must be defined in *Tools* → *Preferences*.

Jana2000 converts M91 and M50 to the input files jobname.hkl and jobname.sir, copies the files to the installation directory of *SIR97* and starts the program. Then it waits until *SIR97* exits and offers to accept or deny the resulting structure. Finally the input files of *SIR97* are deleted. For successful solution correct definition of the symmetry and chemical composition is very important.

Starting of *SIR97* through *Jana2000* is very practical as all conversions (especially between standard and non-standard space group symmetry) are done automatically. Some limitations follow from using only very simple set of instructions for *SIR97* so that in difficult cases *SIR97* must be run independently[1].

[1] For this, we can start SIR97 through Jana2000 and copy the input files out of the SIR97 directory to prevent their deleting. Then we quit SIR97, edit the input file and run SIR97 independently. The resulting ins file can be imported by File → Import structure.

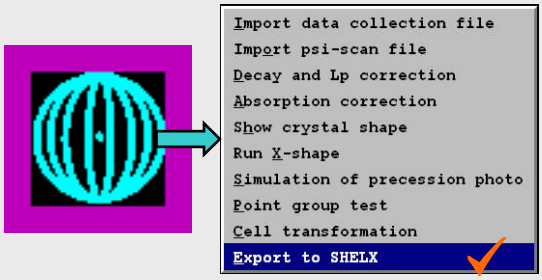
1.2.6.2 Solution with SHELXS

SHELXS cannot be executed directly from *Jana2000*[1]. There are two ways to proceed:

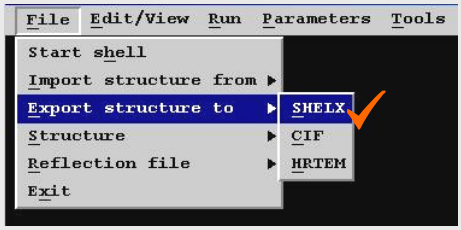
- We can call *Datred* → *Export to SHELX* that transforms M95 to jobname.hkl in *SHELX* format. The file jobname.ins must be prepared by the user.
- If the basic crystal information is defined (i.e. the file M50 exists) we can use File → *Export structure to* → *SHELX* that creates both jobname.hkl and jobname.ins. The commands specific to *SHELXS* must be added by hand to jobname.ins.

In both cases, jobname.hkl contains reflection that are not averaged by symmetry[2]. The resulting structure can be imported back to *Jana2000* by *File* → *Import structure from* → *SHELX*.

Export to SHELX using Datred



Export to SHELX using File → Export



The resulting hkl file:

h	k	l	F	s(F)	Direction cosines
0	1	0	-1.26	16.64	1 0.82990-0.82990 0.08280 0.08310-0.33210 0.33200
0	2	0	852.17	33.00	1 0.82290-0.82300 0.15320 0.15320-0.32930 0.32920
0	3	0	9.64	22.55	1 0.81170-0.81190 0.22310 0.22310-0.32490 0.32470
0	4	0	25.07	32.11	1 0.79620-0.79620 0.29300 0.29330-0.31870 0.31850
0	5	0	14.80	11.30	1 0.77590-0.77610 0.36310 0.36310-0.31060 0.31040
0	6	0	397.73	23.23	1 0.75050-0.75080 0.43310 0.43310-0.30040 0.30020
1	-6	0	22.71	38.31	1-0.24890 0.29980-0.44910-0.41680 0.77130-0.75880
1	-5	0	33.48	11.37	1-0.22240 0.27350-0.38050-0.34570 0.81610-0.80350
1	-4	0	-21.82	28.44	1-0.18790 0.23940-0.31170-0.27460 0.85730-0.84450
1	-3	0	71.31	8.04	1-0.14540 0.19770-0.24310-0.20300 0.89440-0.88160
1	-2	0	-20.95	20.19	1-0.09490 0.14850-0.17430-0.13130 0.92720-0.91410
1	-1	0	861.79	25.72	1-0.03560 0.09320-0.10460-0.05980 0.95500-0.94090
1	0	0	23.27	2.24	1 0.03710 0.03710-0.02370 0.02370 0.97780-0.95970

1.2.6.3 For users that want to skip structure solution

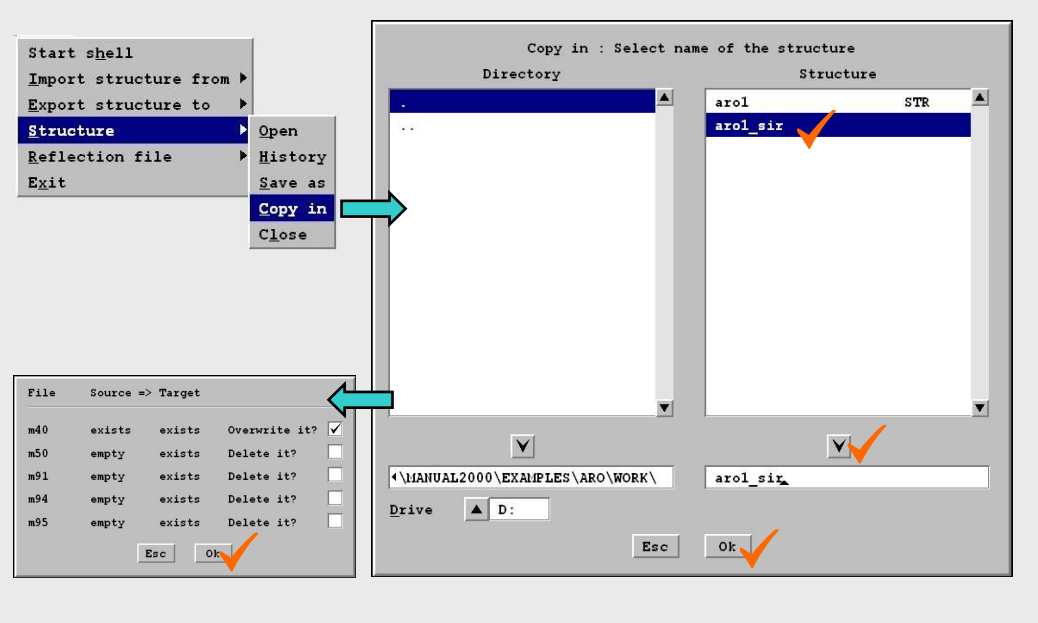
The solution found by *SIR97* can also be downloaded from the Web as **aro1_sir.zip**.[3] The archive contains file aro1_sir.m40 that can be imported into the current job by *File* → *Structure* → *Copy In* command. The tool checks whether the imported files have a counterpart in the files of the current job. Very often, the files in the current job without a counterpart should be deleted in order to avoid inconsistencies. In this

[1] This function will be added in future versions

[2] If M95 does not exist Jana2000 uses M91 for creation of SHELX hkl file. In such case the reflections are averaged by the symmetry used for creation of M91.

[3] http://www-xray.fzu.cz/jana/Jana2000/manual/examples/aro1_sir.zip

case, however, we only want to import M40 and leave the remaining files unchanged[1].



1.2.6.4 Order of atoms returned by direct methods

The order of atoms returned by SIR97 may be different for UNIX and Windows version and it may depend on processor. The user should compare M40 with the copy of M40 given in §1.2.6.3 to ensure that the labeling of atoms is the same. We shall use the labeling further in this chapter.

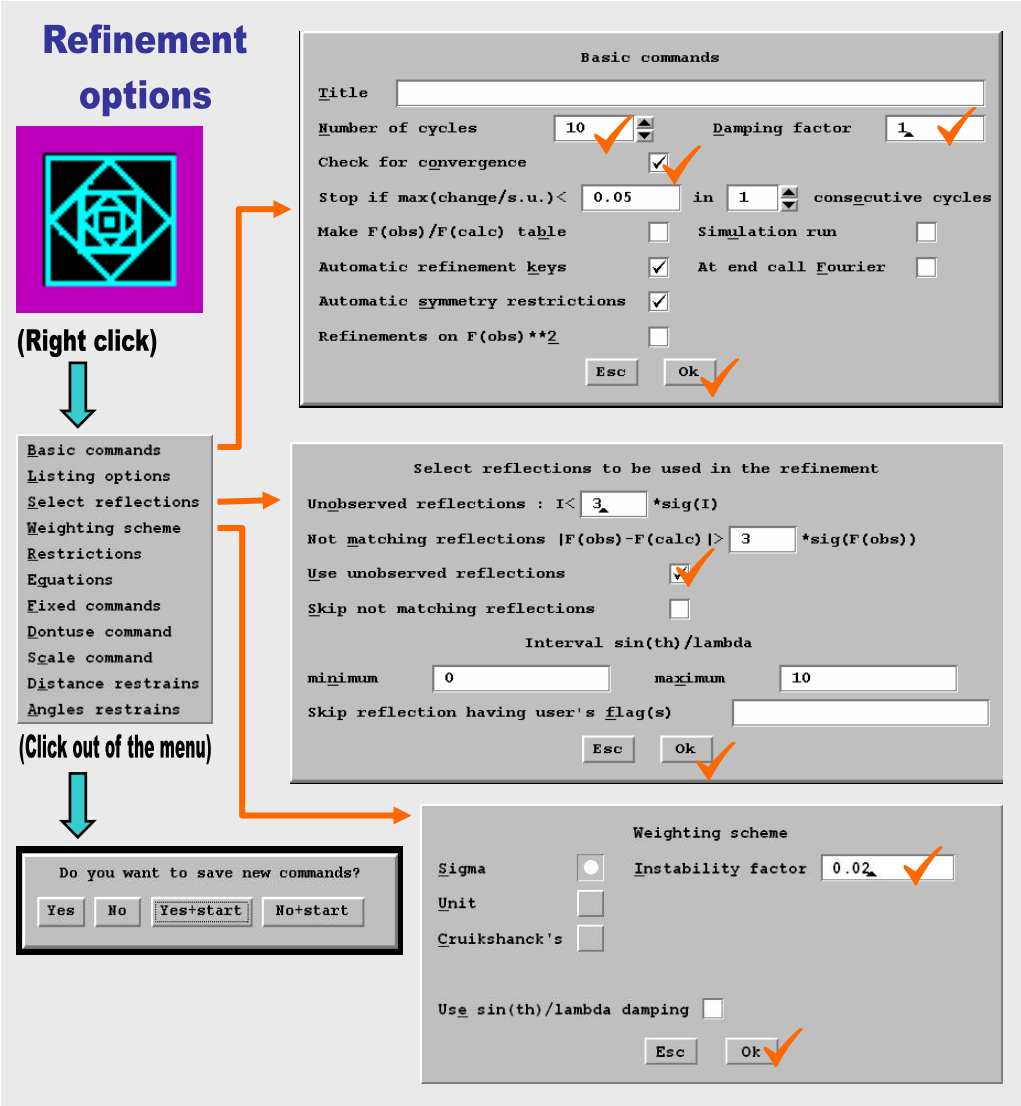
1.2.7 Refinement

The icon of *Refine* has two functions. The left mouse button starts the refinement; the right mouse button starts the *SetCommands* tool for setting refinement options.

1.2.7.1 Refinement options

In *Basic commands* we set 10 refinement cycles with automatic checking of convergence (the program will stops when the convergence limit is reached) and with damping factor one (means no damping). The definition of damping is different of *SHELX*: 1 means no damping, 0 means no changes. We use *Automatic refinement keys* and *Automatic symmetry restrictions*. In *Select reflections* we choose that unobserved reflections will be used for the refinement. In *Weighting scheme* we define the instrument instability 0.02. For the other options, we use their implicit values. Finally, we click with the left mouse button outside the menu to quit the *SetCommands* tool.

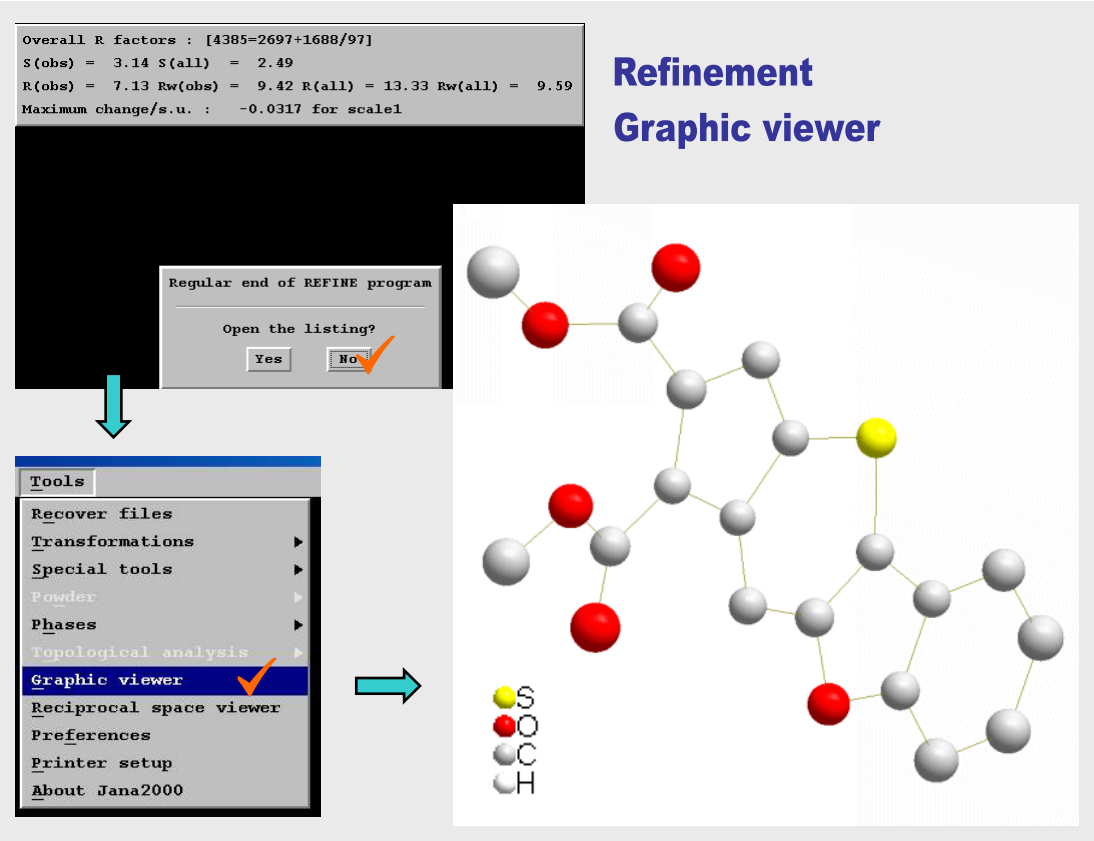
[1] An easier way would be a simple copy using some external file manager. We use the described way in order to introduce the *Copy In* tool.



1.2.7.2 Refinement and viewing of the initial model

As soon as the convergence is reached, *Refine* shows the refinement results on the screen. At the same time, it creates refinement listing with detailed information about the results. The listing is accessible by the *Edit/View* menu.

The resulting structure can be visualized by an external viewer that is started by *Tools* → *Graphic viewer*. The path to the viewer is defined in *Preferences*.



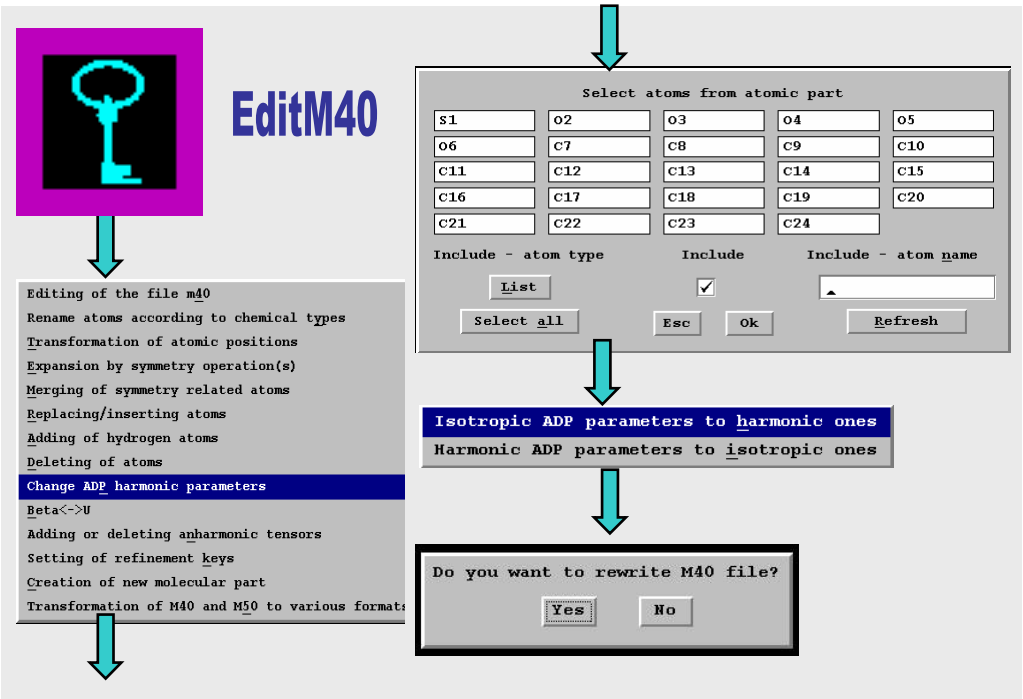
1.2.8 Editing of structure parameters

In the next step, we shall introduce harmonic ADP. To do this, we have to edit structure parameters either in *Parameters* or in *EditM40*.

1.2.8.1 Editing of structure parameters in EditM40

Program *EditM40* is designed to edit parameters for groups of atoms. In most tools of *EditM40* we first select an action (for instance *Deleting of atoms*), then we define the group of atoms for which the action is to be performed and finally we start the action. All changes are made in a temporary file, which is copied to M40 after quitting *EditM40* if the user confirms the changes.

In the following example, we change ADP from isotropic to harmonic ones for all atoms in the structure. Then we can check the made changes by *Edit/View* → *Editing of M40*.



In next two figures, we see how the file M40 looks like before and after the change of ADP. The first 5 lines in M40 are the header lines; in the first line we see number of atoms, in the second line there is overall scale factor. The header is followed by atomic parameters. In this structure every atom has two lines of parameters: Atom name, chemical type, ADP type, site occupation factor, x,y,z in the first line; U11, U22, U33, U12, U13, U23 and refinement keys in the second line. For complicated structures, M40 may take very complex form and it is fully described in the descriptive part of this manual.

M40 before the change, i.e. with isotropic ADP:

```
  24    0    0    0
 1.983745 0.000000 0.000000 0.000000 0.000000 0.000000      100000
 0.000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000      000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000      000000
S1        1  1     1.000000 0.955264 0.209162 0.051917
 0.012531 0.000000 0.000000 0.000000 0.000000 0.000000      0111100000
O2        2  1     1.000000 0.972523 0.314641 0.249966
 0.014128 0.000000 0.000000 0.000000 0.000000 0.000000      0111100000
```

M40 after the change, i.e. with harmonic ADP:

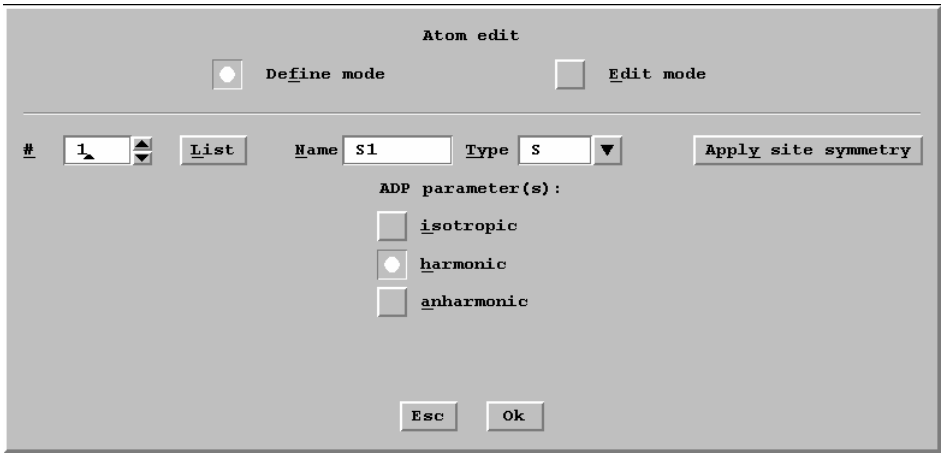
```
  24    0    0    0
 1.983762 0.000000 0.000000 0.000000 0.000000 0.000000      100000
 0.000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000      000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000      000000
S1        1  2     1.000000 0.955264 0.209162 0.051917
 0.012532 0.012532 0.012532 0.000000 0.002881 0.000000      0111111111
O2        2  2     1.000000 0.972523 0.314640 0.249966
 0.014130 0.014130 0.014130 0.000000 0.003248 0.000000      0111111111
```

[1] The numbers at the end of line are refinement keys. They are briefly explained in §1.2.9 .

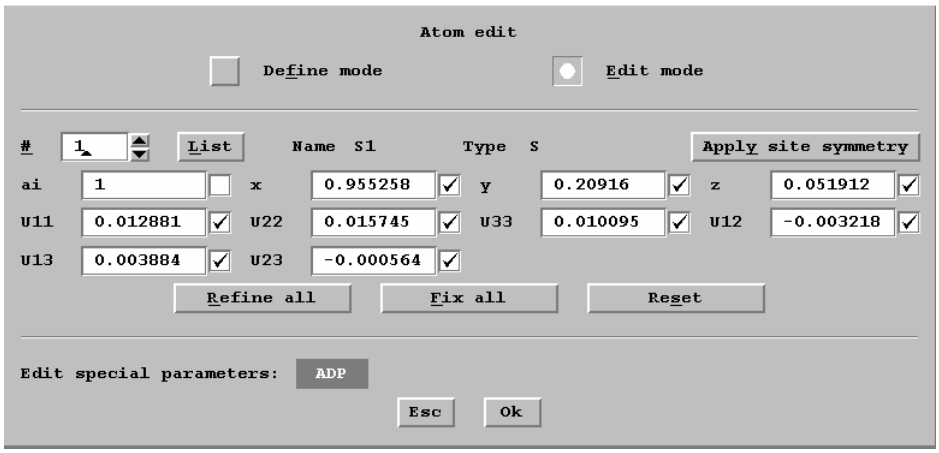
1.2.8.2 Editing of structure parameters by Tools → Parameters

In *Parameters* we first define which atom from M40 is to be edited either by its sequence number or by selecting from the list that can be opened through the *List* button. Then we can select for the atom either *Define mode* or *Edit mode*.

In the *Define mode* we can change chemical type of the atom and type of its ADP[1]. *Apply site symmetry* sets to "0" the refinement keys of parameters that are fixed by symmetry. In our case it has no influence because the automatic refinement keys are used, see § 1.2.9 .



In the *Edit mode* the structure parameters of the given atom and their refinement keys can be edited individually. Setting of refinement keys has again no influence except the *ai*, the site occupation factor, which is never automatic.



1.2.9 Refinement keys

In the next step, we refine the structure with harmonic ADP. The R-value should drop down to approximately 5.3%. We can check in M40 which parameters have been refined.

In our refinement, we use *Automatic refinement keys* and *Automatic symmetry restrictions* (see page 28). This means that the program refines all parameters that are not fixed by the symmetry. The initial refinement keys in M40 are irrelevant as they are overwritten by *Refine*. The exceptions are the scale factors, site occupations and twin volumes. They are implicitly fixed and they are only refined when the user sets

[1] For modulated structures much more possibilities is available.

the corresponding refinement keys to one, for instance by *Tools* → *Parameters*. *Refine* does not change refinement keys of these parameters.
The automatic options are applicable to almost every structure and their use is highly recommended.

M40 after the refinement of harmonic ADP.

```
24    0    0    0
 1.987328 0.000000 0.000000 0.000000 0.000000 0.000000      100000
 0.000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000      000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000      000000
S1        1  2     1.000000 0.955258 0.209160 0.051912
 0.012881 0.015745 0.010095-0.003218 0.003884-0.000564      0111111111
O2        2  2     1.000000 0.972560 0.314516 0.249963
 0.013044 0.019039 0.011576-0.005108 0.002862-0.002132      0111111111
```

1.2.10 Calculation of Fourier maps

After having the structure refined with harmonic ADP, we can calculate difference Fourier map and localize hydrogen atoms. *Fourier* uses the structure factors calculated by *Refine* and saved in M80 as an input. Therefore, it is necessary to run at least zero refinement cycles before starting *Fourier*.

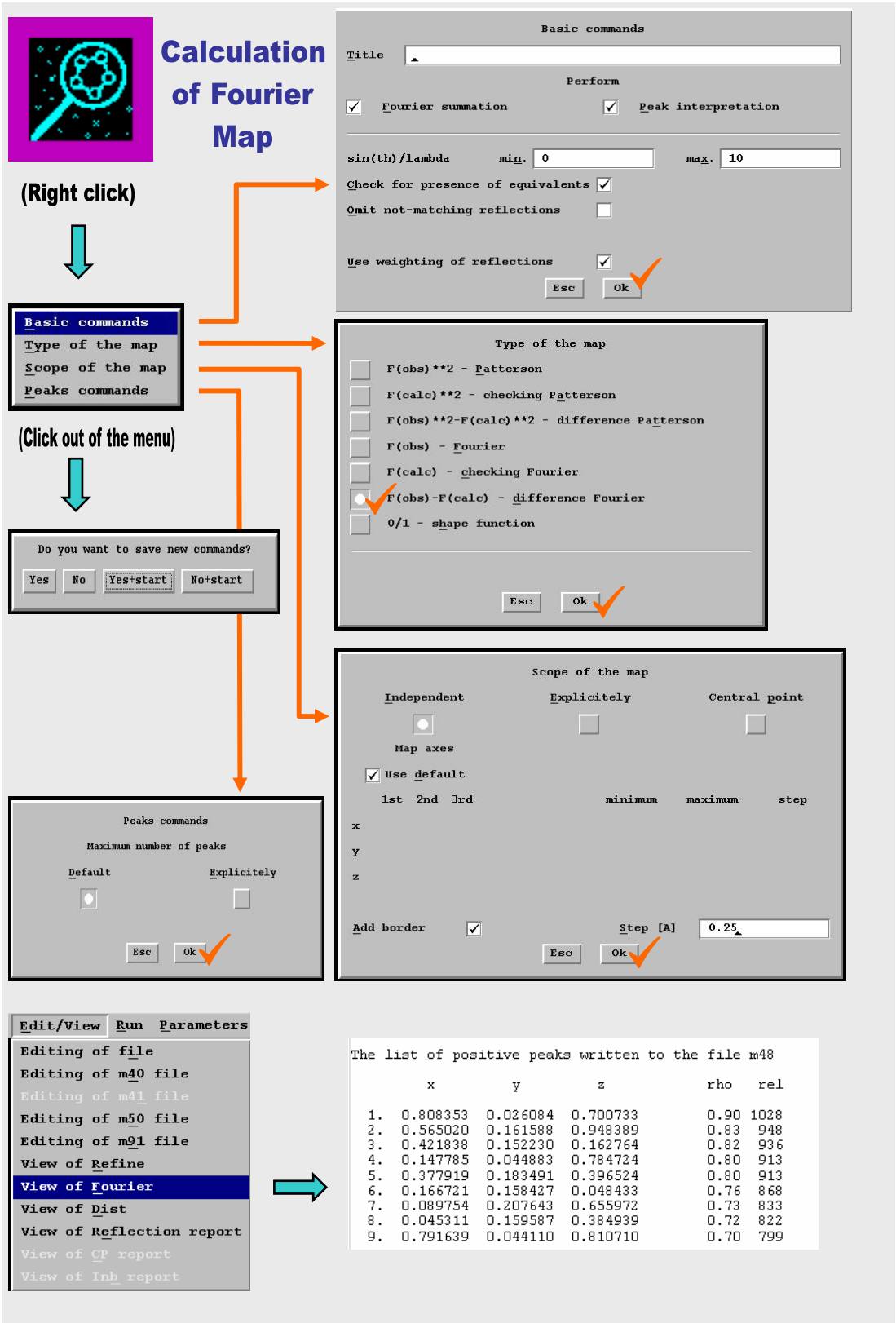
Like in the case of *Refine* the left mouse button starts *Fourier*, while the right mouse button starts the *SetCommands* tool for editing of *Fourier* options. Implicitly, the program makes Fourier calculation and Peak interpretation using reflections (see *Basic commands*), The map is calculated in the independent volume of the elementary cell in the most convenient orientation with step of 0.25 Å (see *Scope of the map*). The program searches for *N+5* largest positive maxima, where *N* is the number of missing atoms calculated from the formula in M50 [1] (see *Peaks commands*). The only option the user has to change in our case is the *Type of the map* that should be *Difference Fourier*.

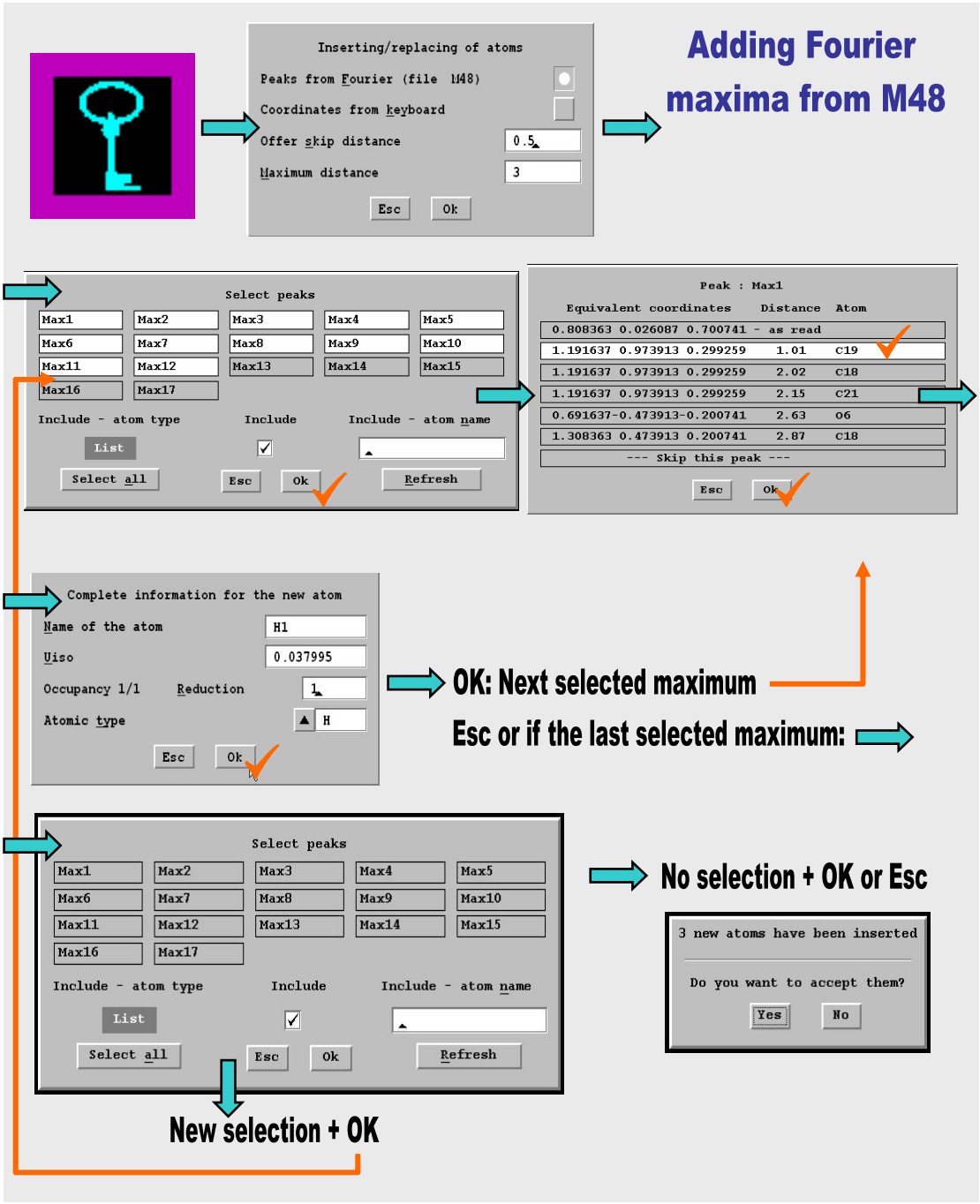
The calculated Fourier map is stored in M81. The *Contour* program plots the two-dimensional sections through the map as contour plots using M81 as an input. Fourier maxima and minima are stored in M48 and M47, respectively. Detailed information about Fourier calculation and found peaks is available in the listing of *Fourier*.

EditM40 can be used for adding Fourier maxima from M48 to M40. The process of calculating Fourier and refining new atoms is repeated until all atoms of the structure are located.

Dist can be used for calculation of distances between atoms and Fourier maxima or minima. Their inclusion to the calculations is controlled in the *Dist* options.

[1] In M40, there are 24 atoms. The formula previously defined through EditM50 is S1O5C18H12, number of formula units equals to 4. The number of interpreted difference peaks will be (36-24)+5 = 17.


Calculation of Fourier Map
(Right click)
Basic commands
Type of the map
Scope of the map
Peaks commands
(Click out of the menu)
Do you want to save new commands?
Yes
No
Yes+start
No+start
Basic commands
Title
Perform
Fourier summation
Peak interpretation
sin(th)/lambda
min.
0
max.
10
Check for presence of equivalents
Omit not-matching reflections
Use weighting of reflections
Esc
Ok
Type of the map
F(obs)**2 - Patterson
F(calc)**2 - checking Patterson
F(obs)**2-F(calc)**2 - difference Patterson
F(obs) - Fourier
F(calc) - checking Fourier
F(obs)-F(calc) - difference Fourier
0/1 - shape function
Esc
Ok
Scope of the map
Independent
Explicitely
Central point
Map axes
Use default
1st 2nd 3rd
minimum
maximum
step
x
y
z
Add border
Step [A]
0.25
Esc
Ok
Peaks commands
Maximum number of peaks
Default
Explicitely
Esc
Ok
Edit/View
Run
Parameters
Editing of file
Editing of m40 file
Editing of m41 file
Editing of m50 file
Editing of m91 file
View of Refine
View of Fourier
View of Dist
View of Reflection report
View of CP report
View of Inb report
The list of positive peaks written to the file m48
x y z rho rel
1. 0.808353 0.026084 0.700733 0.90 1028
2. 0.565020 0.161588 0.948389 0.83 948
3. 0.421838 0.152230 0.162764 0.82 936
4. 0.147785 0.044883 0.784724 0.80 913
5. 0.377919 0.183491 0.396524 0.80 913
6. 0.166721 0.158427 0.048433 0.76 868
7. 0.089754 0.207643 0.655972 0.73 833
8. 0.045311 0.159587 0.384939 0.72 822
9. 0.791639 0.044110 0.810710 0.70 799



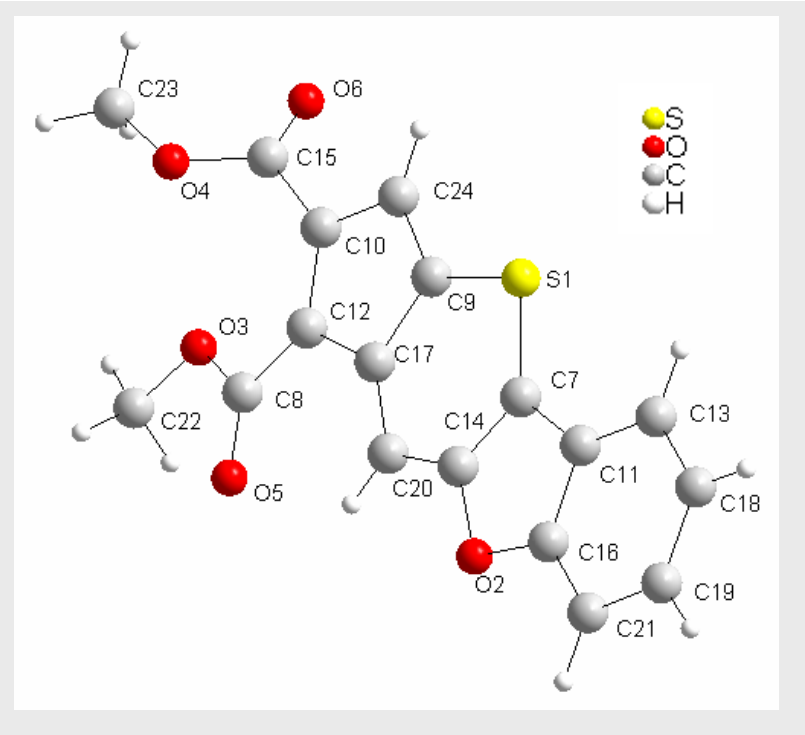
After localization of all relevant difference maxima, the structure should contain 36 independent atoms in M40 and the resulting R factors should be as shown here:

```
Overall R factors : [4385=2697+1688/265]
S(obs) =  1.98 S(all)  =  1.58
R(obs) =  4.63 Rw(obs) =  5.74 R(all) = 10.58 Rw(all) =  5.96
Maximum change/s.u. :    0.0344 for y[C22]
```

1.2.11 Structure interpretation

1.2.11.1 Plotting of the structure

We have already shown in § 1.2.7.2 page 29, that the structure can be visualized by an external plotting program. In this example, we use the plotting program Diamond [3].



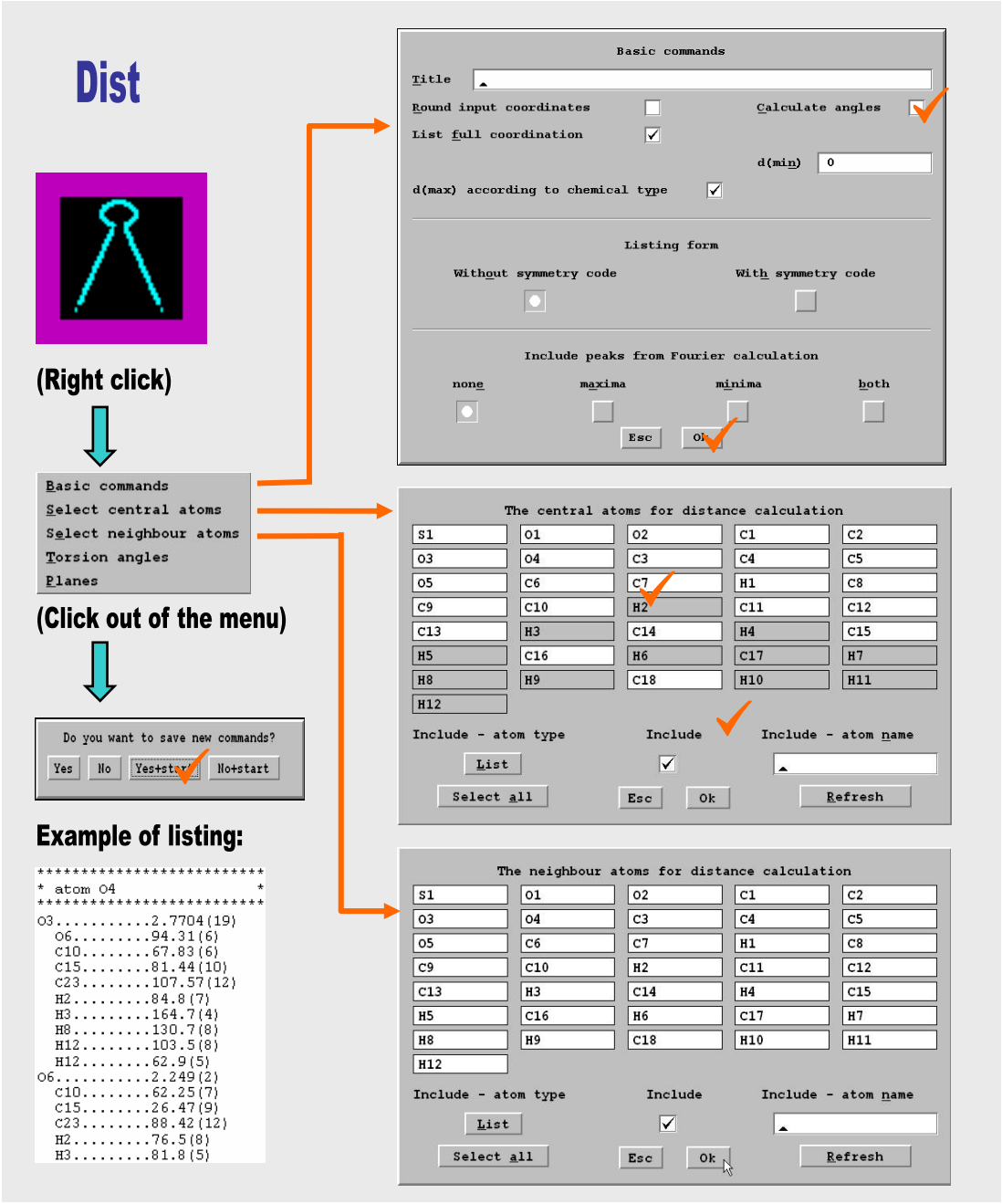
1.2.11.2 Calculation of distances

The distances are calculated by program *Dist*. For a given atom, the distances and angles are listed between *d(min)* and *d(max)* distances. The limits can be defined either independently for each chemical type or equally for all stoms. *D(max)* for chemical types is implicitly set to 3Å when inserting an atom by *EditM40* and it can be changed through *EditM50* in the *Atom form factors* subwindow. *Jana2000* does not use any kind of tables of atomic radii in the distance calculation.

The maxima and minima from Fourier calculation stored by *Fourier* in M47 and M48, respectively, can be included into distances calculation. For these positions, *D(max)* is always set to 3Å.

In the following example, we first set options for the distance calculation through the *SetCommands* tool for *Dist*. The interface enables selection of central and surrounding atoms in order to limit the output to requested information. In the listing shown in the example there is the central atom O4 with coordinated O3, C5, O6, C15 and C24. The nested lines show angles A1-A2-A3, where A2 is the central atom printed in the heading (O4 in this case) while A1 and A3 are some another atoms coordinated to A2; for instance the first angle 68.0º is O3 - O4 - C5, the second value 95.9º belongs to O3 - O4 - O6 etc.

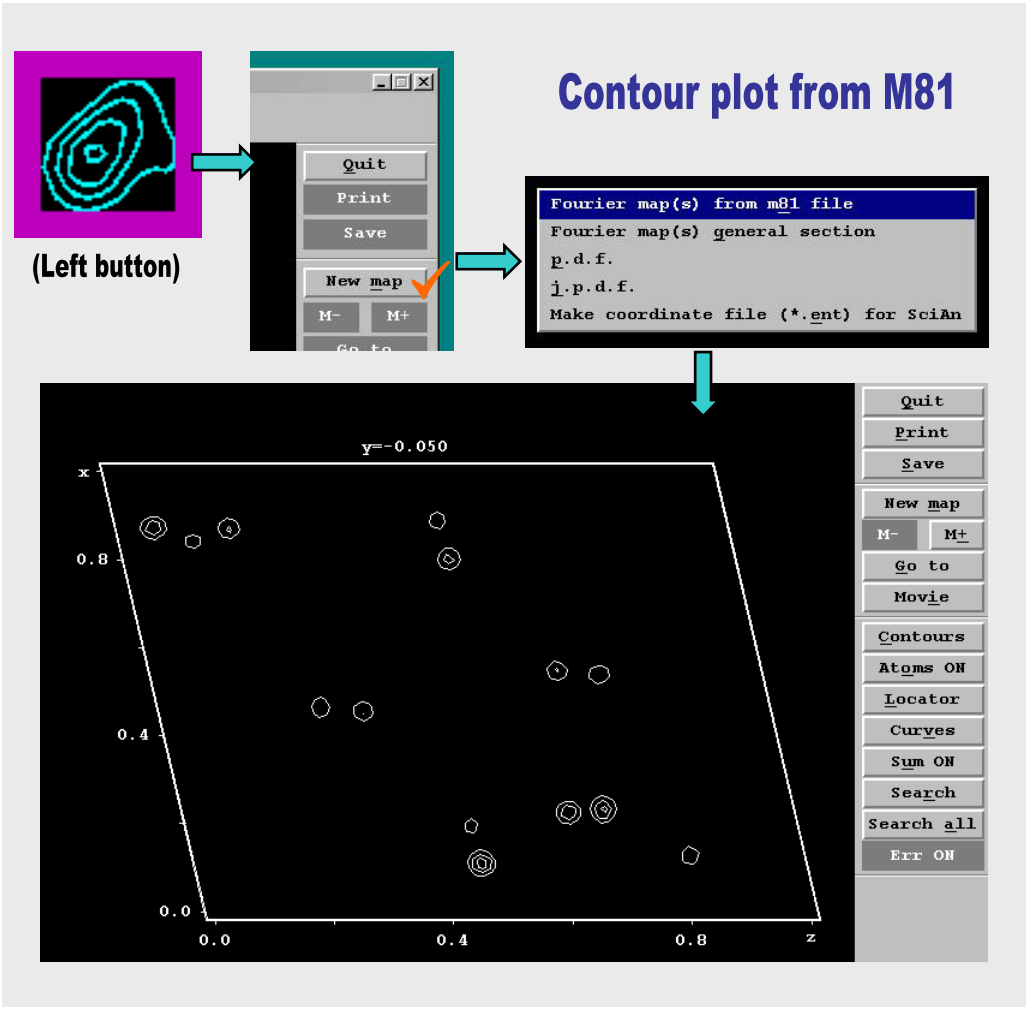
Besides the listing, there is another output of *Dist* stored in M61 in one column format. This listing M61 contains symmetry codes (see § 1.1.7 , page 16).



1.2.11.3 Plotting Fourier map with Contour

Fourier maps can be visualized by *Contour* program. Although plotting of Fourier map is not necessary for solution of this simple structure, we shall nevertheless give two basic examples of *Contour* application. It is a good starting point for § 1.4 where *Contour* plots are important for understanding the structure.

In the first example, *Contour* plots directly sections from M81 pre-calculated by *Fourier*. In this file the Fourier map is stored as a sequence of two-dimensional sections; their orientation and number depends on the *Scope* options (see page 33). In our case, the sections are parallel with the **ac** plane and they are stacked along the **b** axis. *Contour* plots the first section and provides button *M+* and *M-* for moving forward and back in the sections along **b**.



Very often, some special orientation of the sections is required. If the orientation is one of **ab**, **ac** or **bc** it can be defined as *Map axis* in the *Scope* options of *Fourier*, see page 33. For other orientations, there is the *General section* tool available in the *Contour* program that calculates an arbitrary section through the Fourier map using M81 calculated in the independent volume, i.e. using the default parameters of Fourier *Scope*.

In the next example, we calculate a section through one of the rings in our molecule. The plane of the section is defined by three atoms S1, C9 and C7. The first two atoms define the horizontal axis of the section; the third one completes the right-handed system of Cartesian axis with the origin in the first atom.

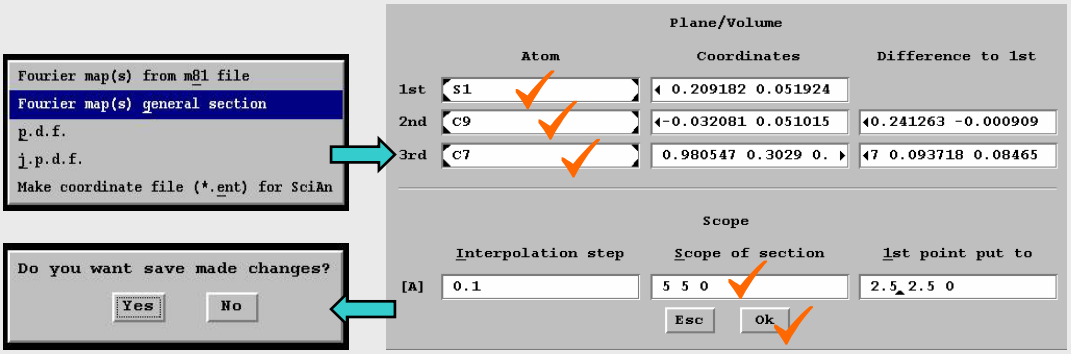
The *Scope*[1] of the section defines (in angstroms) the size of the horizontal, vertical and perpendicular axis, respectively. If the size of the perpendicular axis is greater than zero the program calculates set of equally oriented sections that are stacked along the direction perpendicular to the section plane with the stacking step equal to the *Interpolation step*. In our example, we calculate only one section.

S1 is automatically moved to the centre of the section, i.e. to the point (2.5, 2.5, 0). With this shift, however, the ring is not fully visible. Therefore, the position of S1 is redefined to (1.5, 1.5, 0).

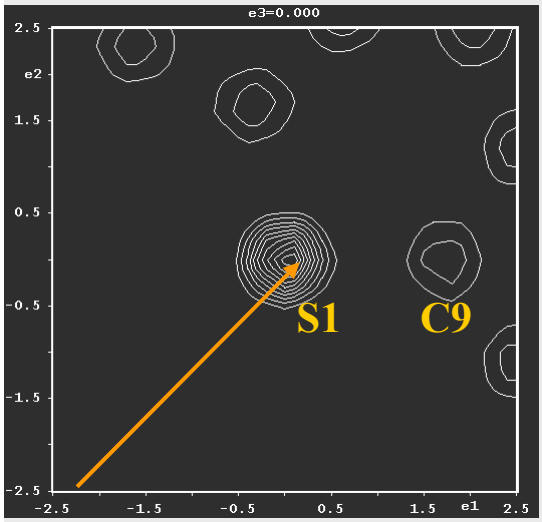
The appearance of curves is influenced by the *Interpolation* step of the general section and by the step used for calculation of the map (see *Step* in the *Scope* options for *Fourier*). For smooth curves, both of them should be 0.1Å or less.

[1] The Scope of Contour general section is not the Scope for calculation of Fourier map.

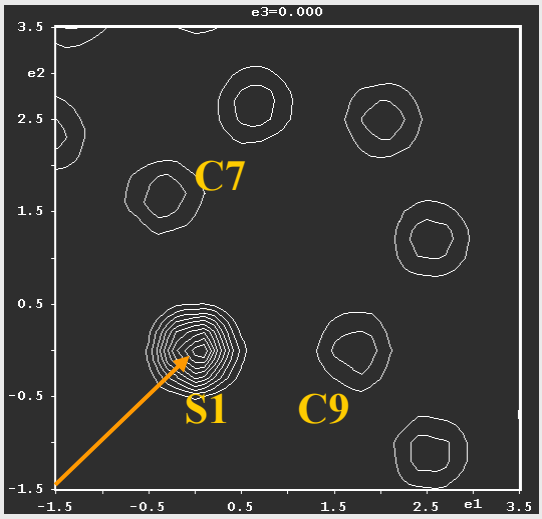
General section

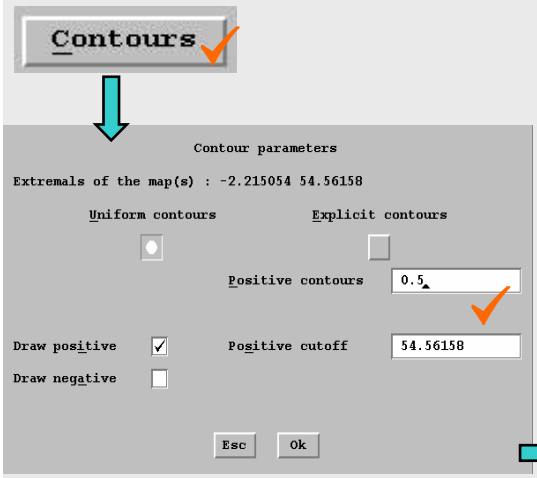


First point to (2.5 2.5 0)

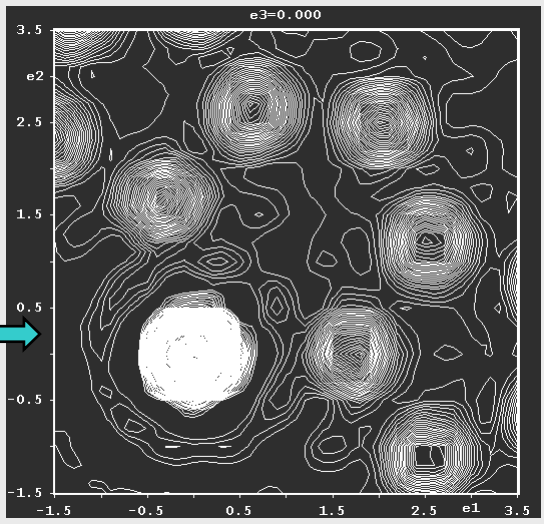


First point to (1.5 1.5 0)





Contour step changed from default to 0.5

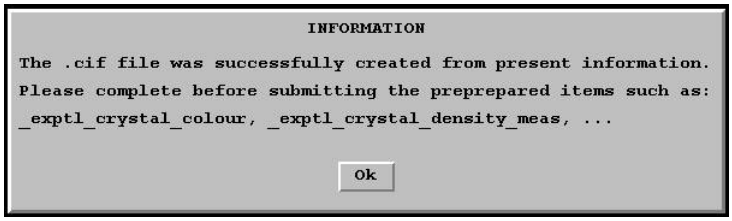


1.2.11.4 Creating CIF output

In the last step, we shall create CIF file through *File → Export structure to → CIF* for publication purposes or as an input to other programs. The tools of *Jana2000* contribute to the file jobname.smr that is used for creation of CIF. If the complete structure solution from the reading of diffractometer files to the final refinement was done in the same directory using the same job name, the smr file will contain all necessary information. Otherwise, before creating CIF some steps must be repeated.

The steps preceding creation of CIF:

- (If the smr file is not reliable,[1] delete it.)
- *Datred:* If we start from the point-detector diffractometer file, repeat the *Decay and LP correction*. If an absorption correction is used, repeat it using the definitive cell contents. Then create new file M91.
- *EditM50:* check if the estimated standard deviations of cell parameters are present.
- *Refine:* check whether there is the instability coefficient introduced in the weighting scheme (see *Weighting scheme* in refinement options, page 28) and run several cycles of refinement using also unobserved reflections (*Select reflections*) with output of F_o-F_c table (*Basic commands*).
- *Fourier*: run zero refinement cycles with unobserved reflections included in the calculation. (see *Select reflections* in refinement options). Then calculate the difference Fourier map using *Weighting of reflections* (see *Basic commands* for *Fourier*). [2]
- *Dist:* set carefully options for *Dist* in order to limit the output to important distances and angles. Then run *Dist*. Repeated runs of *Dist* do not cumulate information in the smr file. The new run overwrites old distances in smr. As calculation of all needed distances and angles in one run of *Dist* is often impossible, the corresponding section in the CIF needs some user editing.
- Run *File → Export structure to → CIF*. If the program has all possible information the only message shown is



1.2.11.5 Making tables for publication

See Appendix G.

[1] Possible reason can be changing of job name or using of M50 that is not consistent with M94.

[2] Large number of unveighted weak reflections may generate large extremes in the Fourier map.

1.3 Standard structure from powder

The objective when implementing powders into *Jana2000* was creation of a unique interface for single crystals and powders. The structure determination from powder data is thus very similar to the work with single crystals. Differences occur mostly at the initial stage, i.e. during reading of data and profile refinement. The powder option as initially introduced in the year 2000 is described in [5].

In this chapter, we present solution of a simple powder structure Sr_2CeO_4 [6] with the following parameters:

Cell parameters	a=6.12Å, b=10.36Å, c=3.59Å
Radiation	Cu 1.5406Å with α2 component filtered out
Monochromator	26.3º (quartz monochromator , 1 0 1 reflection, parallel setting)
Space group	Pbam
Chemical formula	Sr_2CeO_4, Z=2
Profile data format	MAC
Measurement technique	Cylindrical sample (Debye-Scherer)
Absorption factor μr	1.8

The profile data are available in the Jana Web page as **sco1.zip**.[1]

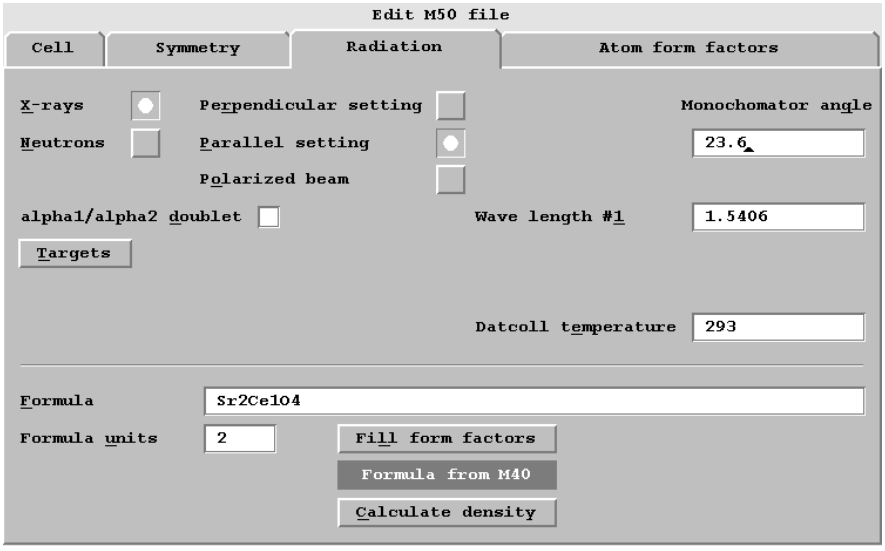
1.3.1 Data preparation

Input: profile data, crystallographic information
Output: M50, M92
The cell parameters must be known as *Jana2000* does not contain any indexing tool.

1.3.1.1 Entering crystal data by EditM50

In the first step, we prepare M50 by entering cell parameters, space group, radiation type, wavelength and atom form factors. We proceed exactly like in the case of single crystal structure, see page 23. Cell parameters, space group and radiation wavelength are used for generation of Bragg positions. The atom form factors will be used later in the structure refinement. Special attention should be paid to proper completion of the *Radiation* form.

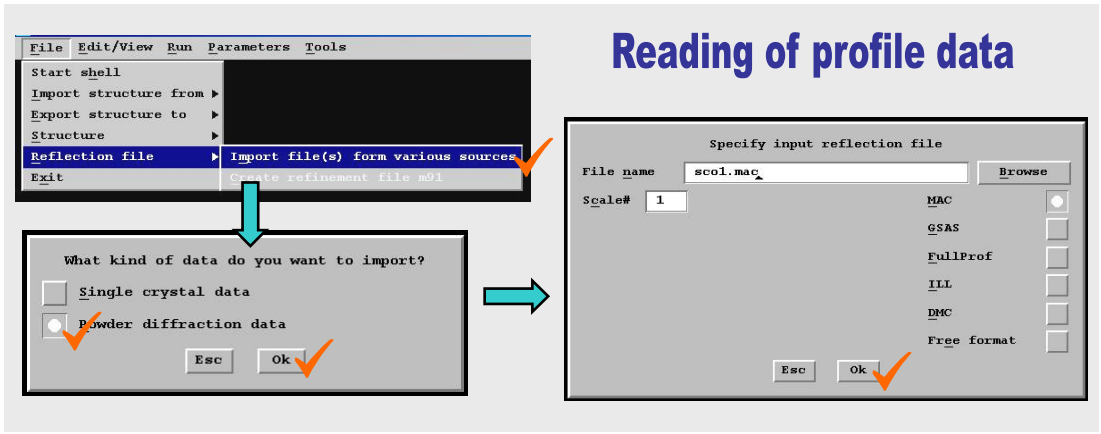
[1] http://www-xray.fzu.cz/jana/Jana2000/manual/examples/sco1.zip



1.3.1.2 Reading of profile data

After having completed the basic crystallographic information we can import the profile data through *File → Reflection file → Import file(s) from various sources*. We choose the MAC format. The imported profile data are saved in M92 that plays the same role like M95 in case of single crystals: it is the common format for experimental powder data used by *Jana2000*.

After importing powder data the powder option of *Jana2000* is activated while the options special for single crystals are disabled.



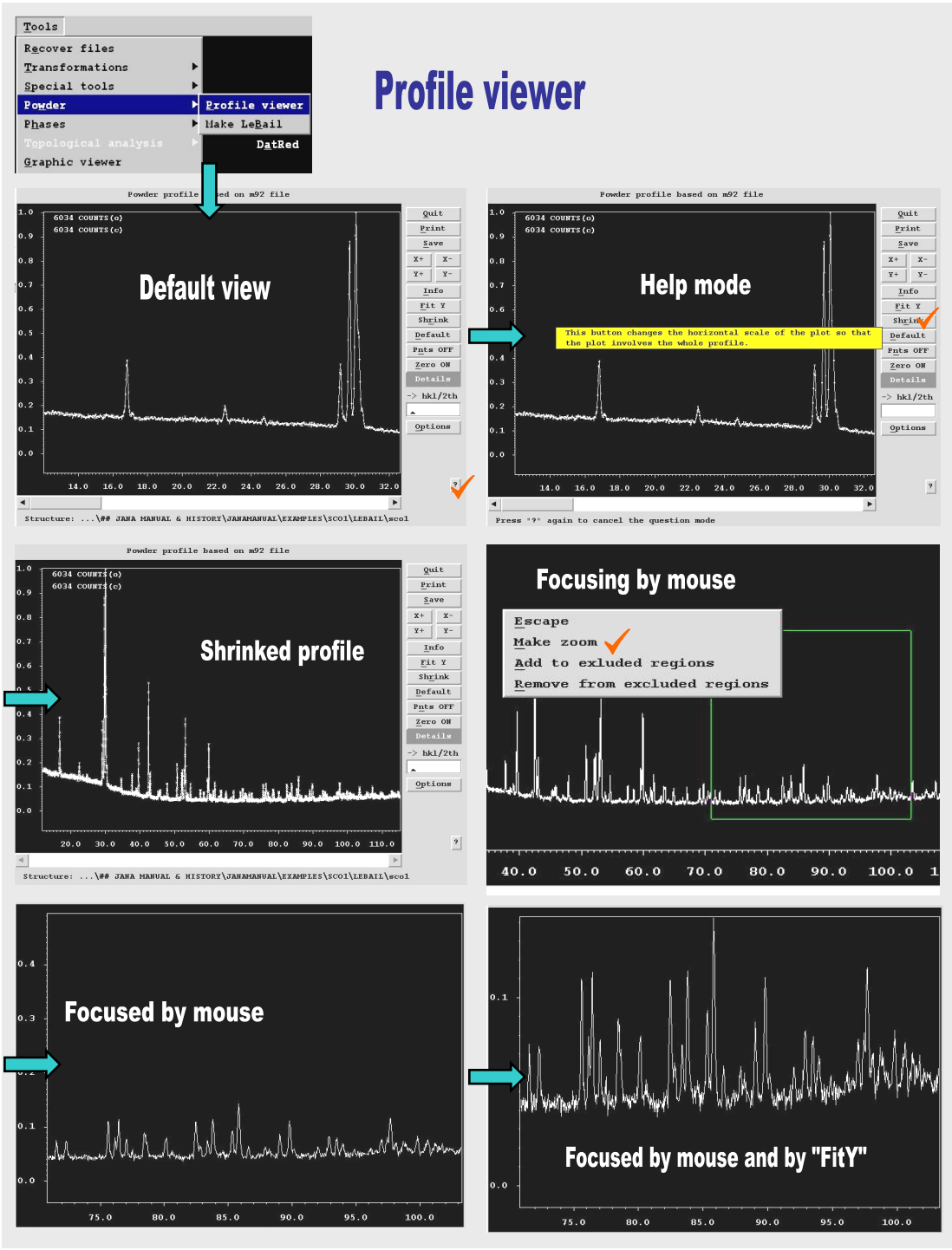
1.3.1.3 Using profile viewer

In *Tools* we can start *Powder → Profile viewer* to plot part of the experimental profile from M92. The buttons on the right are used for navigation through the profile and for setting of the viewer options. The profile viewer is a rather complex tool so and here we shall demonstrate only several basic functions.

Buttons *X+*, *X-*, *Y+* and *Y-* are used for adjusting the scale in the horizontal (X) and vertical (Y) direction. *Shrink* changes both the horizontal and vertical scale to see the complete plot in the viewer window. *Pnts* switches between the default view with visible experimental points and the view where only the polyline connecting the points is visible. The button "*?*" starts a help mode that prints a short comment for each button that is pressed.

It the next scheme, we first import the profile data and plot the profile. Then the help mode is demonstrated for the case of button *Shrink* and the whole profile is shown as the result of pressing *Shrink*. We can select an area in the plot using a

rectangle drawn by the left mouse button. If we then click the right button in the rectangle, a context menu appears with list of operations that are possible on the selected area. We choose *Make zoom* that adjusts the horizontal scale to fit the rectangle in the whole window. The vertical scale remains unchanged until we press *Fit Y*.



1.3.2 Refinement of profile parameters

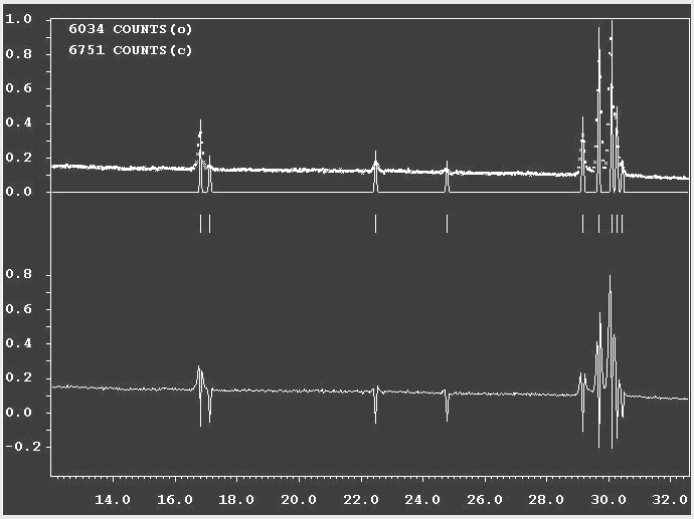
Profile parameters are refined by *Refine*. The output files are M41 (the profile parameters), M91 (input for *EXPO*) and M80 (input for *Fourier*).

1.3.2.1 Le Bail decomposition

Tools → *Powder* → *Make LeBail* starts the Le Bail decomposition. The output files are jobname.prf and jobname.m91. In M91, there are results of the peak decomposition, i.e. the squares of structure factors and their *e.s.d's*. The prf file contains the calculated profile based on profile parameters and Bragg positions. M91 can be used for solution of the phase problem by *EXPO* (see later) or for calculation of the Patterson map[1].

In this stage, however, the profile parameters have not been yet refined. Implicitly the only non-zero profile parameter is *GW=5*, so that the program generates very narrow peaks based on this parameter. In *Tools* → *Powder* → *Plot powder profile* we can compare the calculated (prf) and experimental (M92) profile.

The initial Le Bail decomposition



File M91

h	k	l	m	n	o	I	s(I)			
0	2	0	0	0	0	825.0	1.0	1	0	1
1	2	0	0	0	0	823.8	1.0	1	0	1
0	0	1	0	0	0	1518.1	1.0	1	0	1
2	0	0	0	0	0	5236.9	1.0	1	0	1
1	3	0	0	0	0	6546.1	1.0	1	0	1
1	1	1	0	0	0	3332.1	1.0	1	0	1
0	2	1	0	0	0	3245.9	1.0	1	0	1
2	1	0	0	0	0	1504.9	1.0	1	0	1
1	2	1	0	0	0	480.1	1.0	1	0	1
2	2	0	0	0	0	1008.0	1.0	1	0	1
0	4	0	0	0	0	2893.1	1.0	1	0	1
1	4	0	0	0	0	1921.2	1.0	1	0	1
2	0	1	0	0	0	1034.0	1.0	1	0	1
1	3	1	0	0	0	637.8	1.0	1	0	1
2	3	0	0	0	0	996.8	1.0	1	0	1
2	1	1	0	0	0	1725.9	1.0	1	0	1
2	2	1	0	0	0	4116.9	1.0	1	0	1
0	4	1	0	0	0	2676.1	1.0	1	0	1

1.3.2.2 Powder parameters

Powder parameters can be edited using *Parameters* → *Powder*. This starts a tool similar to *EditM50* that contains all profile parameters. Their values are stored in M41 that is analogy of M40.

In the following scheme, there are copies of all subwindows of *Powder parameters* with their default values. Their refinement keys are all set to zero so that no powder parameters are refined.

Basic subwindow contains information about radiation. The numbers edited here are saved not only in M41 but also in M50 so that the changes are reflected in *Radiation* subwindow of *EditM50*. Conversely, the changes made in the *Radiation* subwindow of *EditM50* will be also visible in the *Basic* subwindow of *Powder parameters*. The same rule holds for the *Cell* subwindow of *Powder parameters* that corresponds to the *Cell* subwindow of *EditM50*.

[1] Fourier requires the file m80 as an input. Calculation of Patterson map is the only case when M80 can be replaced by M91.

Profile subwindow contains the initial values of profile parameters. The only non-zero parameter is *GW* - the one that has been used in the initial Le Bail decomposition. *Cutoff* determines points of the profile that contribute to a given Bragg position.

Asymmetry and *Sample* subwindows contain parameters of the profile asymmetry, preferred orientation and absorption. *Corrections* subwindow contains background and shift parameters.

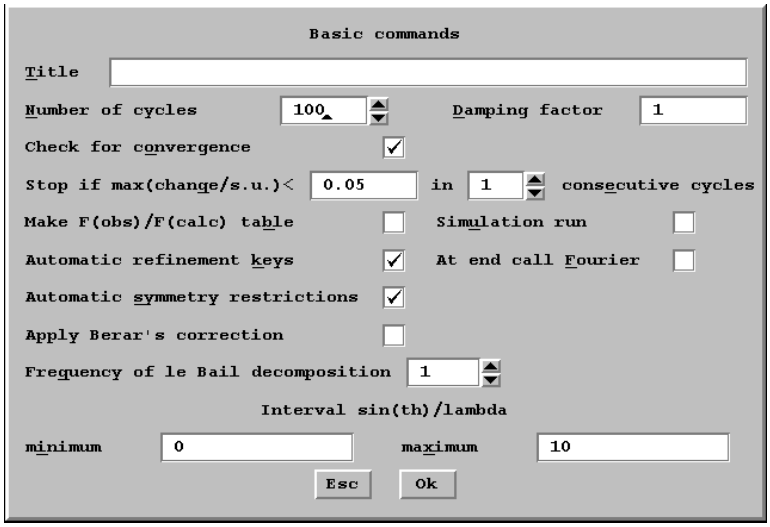
1.3.2.3 Refinement options

Prior to the refinement of the profile parameters *Refine* executes the Le Bail decomposition in order to extract intensities that are necessary for the calculation[1]. Then it refines the profile parameters using the extracted intensities in one or more refinement cycles. The number of refinement cycles between two consecutive Le Bail decompositions is an important parameter. If it is one (i.e. the Le Bail decomposition is executed prior to each refinement cycle) it may cause instability of the refinement. On the other hand, too large number slows down the refinement and must be coordinated with number of refinement cycles to avoid false convergence (see later). We recommend setting the frequency of Le Bail decomposition to one and change it only if the refinement is unstable.

The *Basic commands* subwindow of the refinement options looks similarly like in case of single crystal refinement except two points: *Frequency of Le Bail decomposition* and *Apply Berar's correction*.

Frequency of Le Bail decomposition must be less than *Number of cycles* and *Number of consecutive cycles* used in *Check for convergence*. This is because the refinement may completely converge before a new Le Bail decomposition is calculated.

Berar's correction is estimated during the refinement and it is applied to standard uncertainties of all refined parameters (profile, elementary cell and structure). Usually it leads to larger values that are more realistic. The correction does not influence the refinement itself.



1.3.2.4 Refinement of background parameters

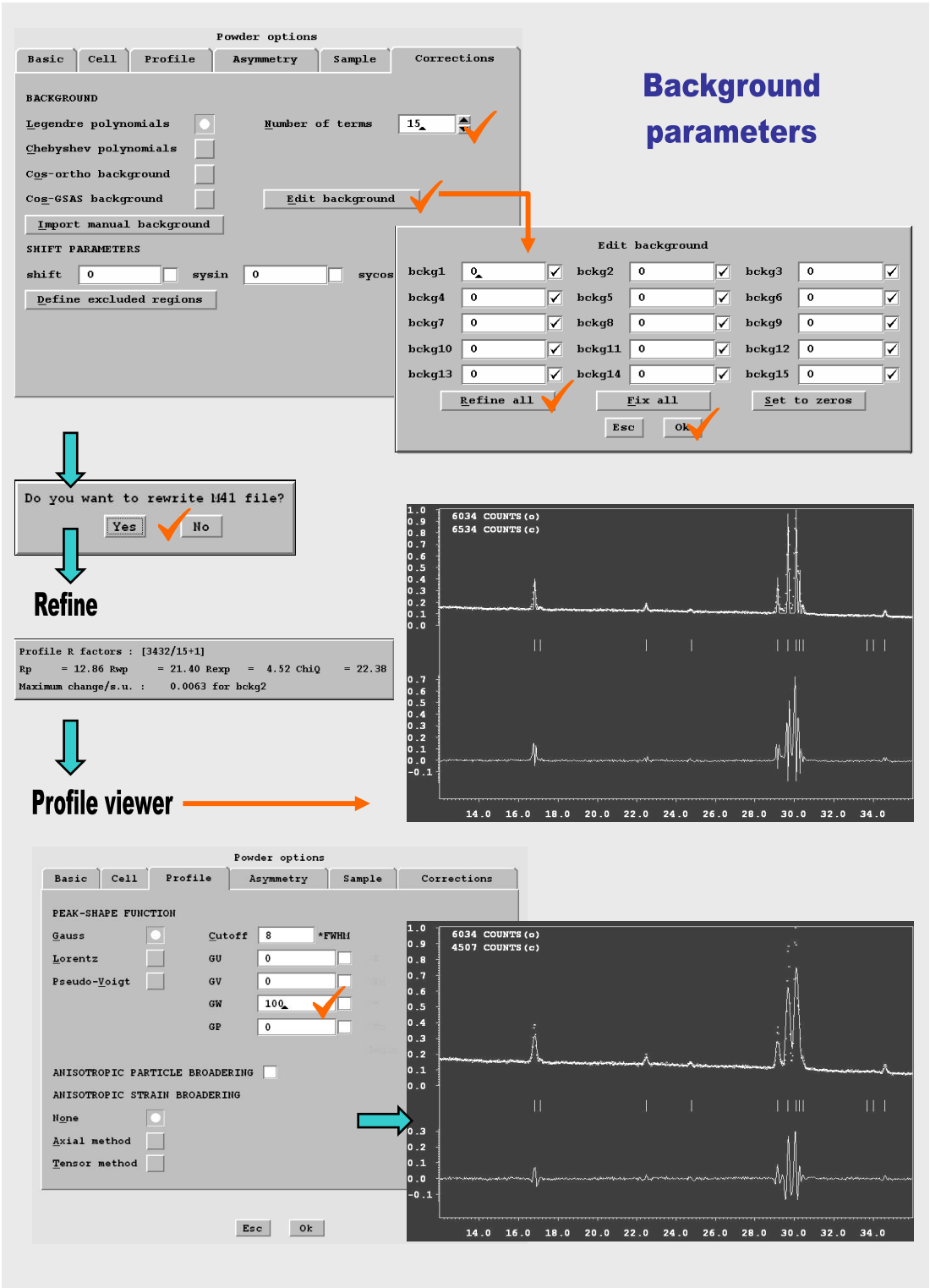
Background parameters should be refined first. The background is usually modeled by Legendre polynomials using from 5 to 15 terms. Here we shall refine 15 terms. No initial values of the terms are necessary. Their refinement keys must be set to "1" using *Edit backlground* in *Powder options* → *Corrections*. After the refinement, the *Rp* factor will drop to approximately 13%. Then we can visualize the new calculated profile by *Profile viewer*.[2]

In the following scheme, we can see the sharp peaks generated by *GW* = 5 are now shifted onto the refined background. Usually this is a good starting point for

[1] If there is already a structure available, the intensities are calculated from the structure. At the end, Refine makes the peak decomposition and creates M80 for calculation of Fourier maps. For compatibility with some tools, it also creates M91.

[2] The prf file with calculated profile is only created when Refine finishes regularly. With Refine interrupted by Cancel button, no prf file is created and Profile viewer plots only the experimental profile from M92.

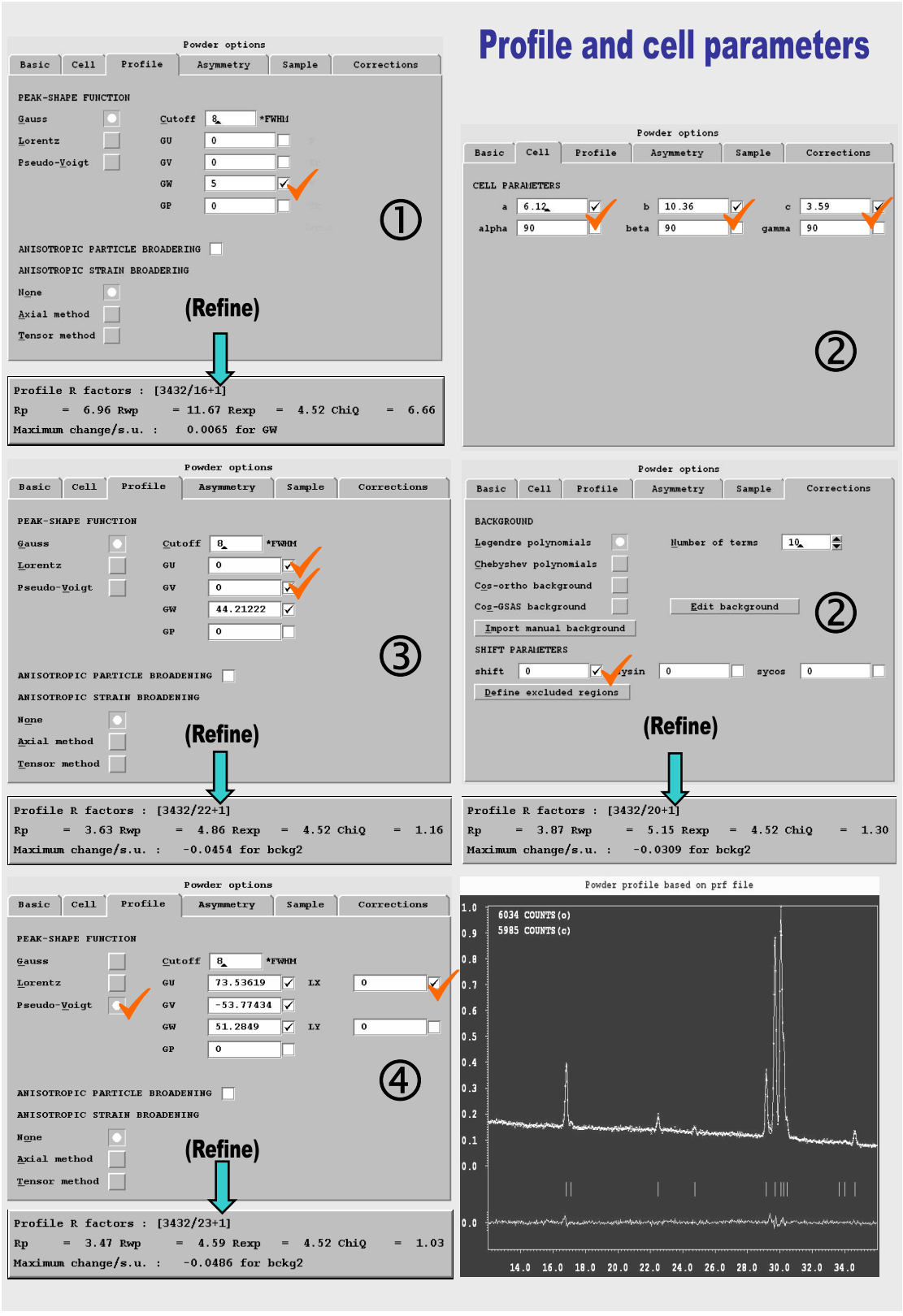
refinement of profile parameters. In some special cases it may be better to find more favorable starting point by changing *GW* with *Parameters* → *Powder* → *Profile*, calculating Le Bail decomposition through *Tools* → *Powder* → *Make Le Bail* and inspecting the resulting profile with *Profile wiever*. In the scheme below we show a plot of the calculated profile for *GW = 100*.



1.3.2.5 Refinement of profile, cell and shift parameters

In the next step, we refine the parameter *GW*. The refinement should converge to R_p about 7%. Then we proceed with refinement of cell parameters and zero shift

(subwindow *Cell* and *Corrections*, $R_p \approx 4\%$) and refinement of *GU* and *GV* (subwindow *Profile*). We change type of the profile function from Gaussian to Pseudo-Voigt and refine *LX*. The final value of R_p will be about 3.5%.



1.3.3 Refinement of structure

1.3.3.1 Solution of the structure by EXPO

EXPO [2] performs the extraction of the structure factor amplitudes from the powder pattern by using the Le Bail algorithm. The extracted integrated intensities are processed by Direct Methods in order to solve the structure. *Jana2000* starts *EXPO* as an external program that must be downloaded and installed separately by the user. The path to *EXPO* must be defined in *Tools → Preferences*. *EXPO* is used in a mode that skips the profile decomposition and uses the intensities extracted by *Jana2000*.[1]

EXPO can be called through *Run* menu. *Jana2000* saves extracted intensities to *EXPO* input file jobname.rfl and prepares the crystallographic information and *EXPO* control commands[2] in jobname.exp. Both input files are created in the directory where *EXPO* is installed. Then *Jana2000* starts *EXPO* and waits until the external program exits. After confirmation, *Jana2000* reads the results and deletes input files.

The advantage of starting *EXPO* through *Jana2000* is that all conversions between *EXPO* and *Jana2000* are done automatically. As *EXPO* accepts only standard space groups *Jana2000* converts some non-standard groups before starting *EXPO* and transforms the results back to the original setting. The disadvantage is that *Jana2000* uses only very simple set of instructions for *EXPO*. However, it is sufficient for most cases as *EXPO* is designed for fully automatic run.

1.3.3.2 For users that want to skip structure solution

The solution that would be created by *EXPO* can also be downloaded as **sco1_expo.zip**.[3] The archive contains file sco1_expo.m40 that can be imported into the current job by *File → Structure → Copy In* command (see also page 27).

1.3.3.3 Structure refinement

In the next step, we shall refine the structure model created by *EXPO*. Unlike in the profile refinement there is no option for frequency of Le Bail decomposition because the intensities are now calculated from the structure model. The Le Bail decomposition is only activated when *Make only profile matching* is used.

In the refinement, we do not fix any previously refined profile parameter; they should be refined together with structure parameters. After the refinement, we shall see relatively good agreement factors but the isotropic ADP's will be very small or negative. This is caused by missing absorption correction.

Finally, we can try whether refinement of harmonic ADP is reasonable. The refinement yields acceptable harmonic parameters for Sr1 Ce1 and O2 but for O1 they are not positive definite.

In the later stage of the refinement, we can enable *Apply Berar's correction* to get more realistic standard uncertainties in the distances calculation.[4]

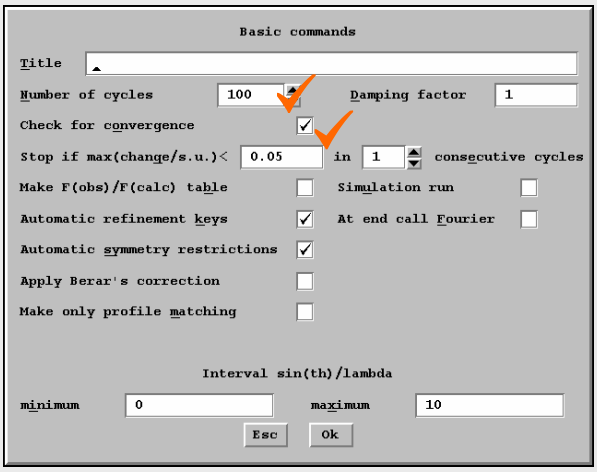
---

[1] In the future export of the powder profile to EXPO will be also possible.

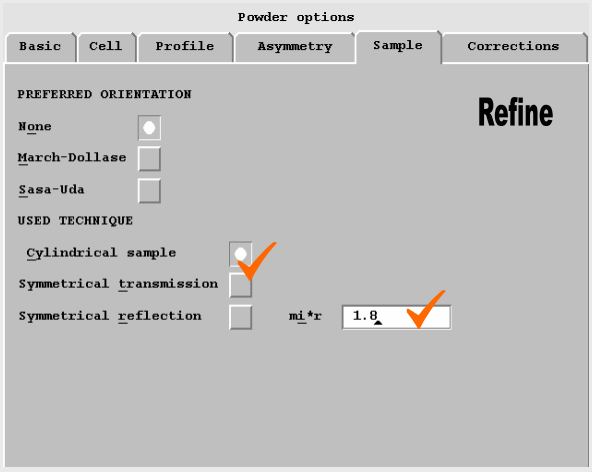
[2] With the commands prepared by Jana2000 EXPO skips extraction of intensities (i.e. the EXTRA program) and uses the intensities supplied by Jana2000.

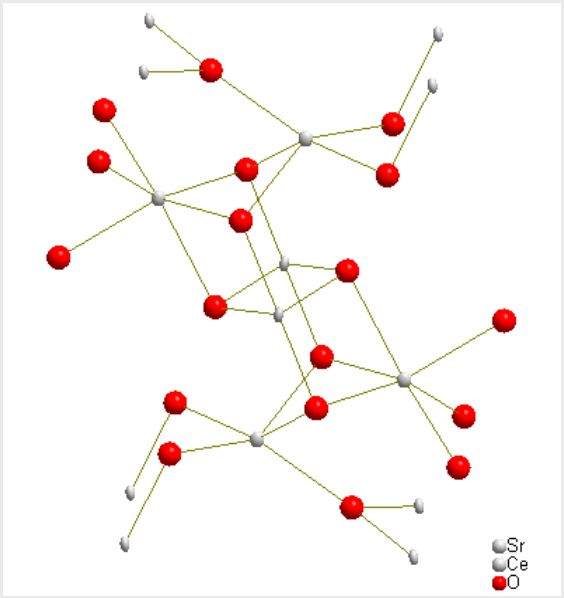
[3] http://www-xray.fzu.cz/jana/Jana2000/manual/examples/sco1_expo.zip

[4] Application of this correction at the beginning of the refinement could bias the automatic recognition of large changes of the scale factor that should lead to repeating of the refinement cycle with new scale without changing the other parameters.



Absorption correction





Structure Refinement

```
Overall R factors : [186=159+27/11]
R(obs) =  3.52 Rw(obs) =  2.54 R(all) =  4.01 Rw(all) =  2.61
Profile R factors : [3432/18+11]
Rp     =  3.84 Rwp     =  5.02 Rexp    =  4.52 ChiQ    =  1.24
Maximum change/s.u. :    0.0401 for x[01]
```

M40 before absorption correction

```
   4    0    0    0
 0.205928 0.000000 0.000000 0.000000 0.000000 0.000000
 0.000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
Ce1        2  1     0.250000 0.000000 0.000000 0.000000
-0.000825 0.000000 0.000000 0.000000 0.000000 0.000000
Sr1        1  1     0.500000-0.063179-0.320225-0.500000
 0.001073 0.000000 0.000000 0.000000 0.000000 0.000000
O1         3  1     0.500000 0.143546-0.193567 0.000000
-0.001956 0.000000 0.000000 0.000000 0.000000 0.000000
O2         3  1     0.500000-0.225932-0.045928-0.500000
 0.009627 0.000000 0.000000 0.000000 0.000000 0.000000
```

```
Overall R factors : [186=159+27/11]
R(obs) =  3.70 Rw(obs) =  2.91 R(all) =  4.18 Rw(all) =  2.97
Profile R factors : [3432/18+11]
Rp     =  3.93 Rwp     =  5.13 Rexp    =  4.52 ChiQ    =  1.29
Maximum change/s.u. :    0.0232 for Uiso[Sr1]
```

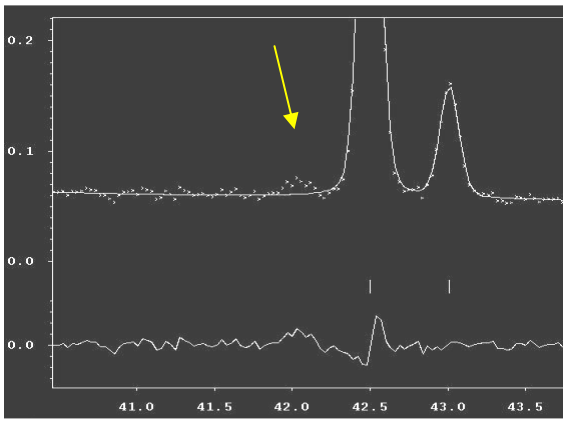
M40 after absorption correction

```
   4    0    0    0
 0.835478 0.000000 0.000000 0.000000 0.000000 0.000000
 0.000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
Ce1        2  1     0.250000 0.000000 0.000000 0.000000
 0.019607 0.000000 0.000000 0.000000 0.000000 0.000000
Sr1        1  1     0.500000-0.063340-0.320221-0.500000
 0.021845 0.000000 0.000000 0.000000 0.000000 0.000000
O1         3  1     0.500000 0.143255-0.193322 0.000000
 0.019616 0.000000 0.000000 0.000000 0.000000 0.000000
O2         3  1     0.500000-0.225864-0.046377-0.500000
 0.033073 0.000000 0.000000 0.000000 0.000000 0.000000
```

1.3.4 Multiphase refinement

Jana2000 can refine up to five powder phases[1] together. Here we present adding and refinement of the second phase.

In the paragraphs 1.3.1 - 1.3.3 we have refined the dominating phase in *sco1*, Sr_2CeO_4. Careful examination of the calculated versus observed profile reveals there are small undescribed peaks, for instance around 42º2θ. This is because there is an admixture of $SrCeO_3$ in the sample with crystal data known from other experiments and summarized in the following table.



Cell parameters	a=6.148Å, b=8.586Å, c=6.010Å, α=β=γ=90º		
Space group	Pnma		
Chemical formula	SrCeO3, Z=4		
Structure			
Ce	0.000000	0.000000	0.000000
Sr	0.063373	0.679763	0.500000
O1	0.857028	0.805629	0.000000
O2	0.225611	0.955184	0.500000

Important limitation

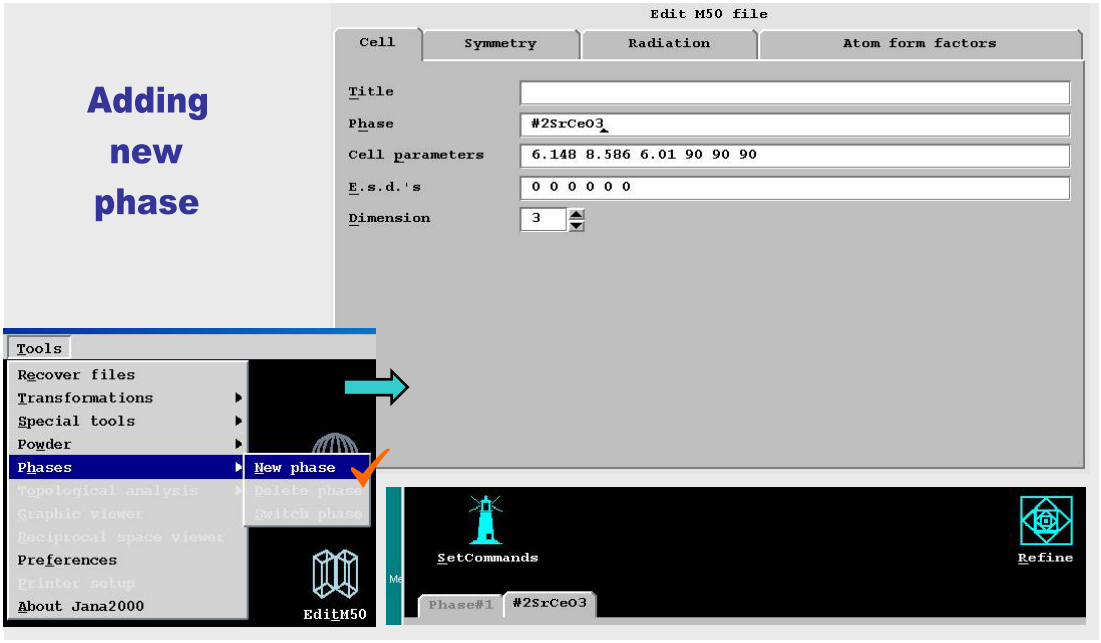
The multiphase option is possible either for a profile (Le Bail) refinement or for Rietveld refinement. The two types of refinement cannot be mixed. If we refine powder and structure parameters of the first phase (Rietveld refinement), the new phase must be added together with its structure to allow the same type of the refinement. On the other hand, if we refine only powder parameters of the first phase (Le Bail refinement), the new phase must be identified only by cell parameters and the space group.

1.3.4.1 Adding new phase

New phase can be added through *Tools* → *Phases* → *New Phase*. This starts the *EditM50* dialogue for setting of the basic crystal information for the new phase. The *Phase* textbox should contain a short (eight characters) phase identifier. In *Radiation* subwindow, the wavelength and the radiation type are already defined as they have been taken from the previous phase. After finishing of *EditM50* the thumbnails with phase identifiers will appear in the left lower corner of the *Jana2000* basic window. They can be used for switching between phases.

We switch to the new phase and enter its structure (*EditM40* → *Replacing/inserting atoms*). The atom names must be unique for all phases. For instance, if there is an atom S1 in the first phase this name is not allowed in the second phase.

[1] This limit can be changed during program compilation.



As soon as the new phase is added the basic files M40, M41 and M50 acquire multiphase organization with separate data sections for both phases.

M40 after adding the new phase

This is volume fraction of the new phase

```
    4    0    0    0
    4    0    0    0
 0.843921 0.000000 0.000000 0.000000 0.000000 0.010000      100000
 0.000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000      000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000      000000
Ce1       2  1     0.250000 0.000000 0.000000 0.000000
 0.019607 0.000000 0.000000 0.000000 0.000000 0.000000      0000100000
Sr1       1  1     0.500000-0.063340-0.320221-0.500000
 0.021847 0.000000 0.000000 0.000000 0.000000 0.000000      0110100000
O1        3  1     0.500000 0.143255-0.193323 0.000000
 0.019617 0.000000 0.000000 0.000000 0.000000 0.000000      0110100000
O2        3  1     0.500000-0.225863-0.046377-0.500000
 0.033078 0.000000 0.000000 0.000000 0.000000 0.000000      0110100000
Ce_b      2  1     0.500000 0.000000 0.000000 0.000000
 0.037995 0.000000 0.000000 0.000000 0.000000 0.000000      0000000000
Sr_b      1  1     1.000000 0.063373 0.679763 0.500000
 0.037995 0.000000 0.000000 0.000000 0.000000 0.000000      0000000000
O1_b      3  1     1.000000 0.857028 0.694371 0.000000
 0.037995 0.000000 0.000000 0.000000 0.000000 0.000000      0000000000
O2_b      3  1     1.000000 0.725611 0.544816 0.000000
 0.037995 0.000000 0.000000 0.000000 0.000000 0.000000      0000000000
```

M41 after adding the new phase

```
bckgtype 1 bckgnum 15 manbckg 0 wtlebail 1
absor 1 mir 1.8
phase Phase#1
proffun 3 asymm 0 strain 0 cutoff 8
phase SrCeO3
proffun 3 asymm 0 strain 0 cutoff 8
end
************************************************************************
# Shift parameters - zero, sycos, sysin
 0.323450 0.000000 0.000000                                  100
# Background parameters
 407.3499-268.6363 312.9955-104.7968-27.48167 61.88438       111111
-47.05416-7.195762 39.71324-30.45667 19.92561 3.898507       111111
-13.68987 1.227813-4.748011                                  111
### phase Phase#1
# Cell parameters - a,b,c,alpha,beta,gamma
 6.120009 10.35531 3.596630 90.00000 90.00000 90.00000       111000
# Gaussian parameters - U,V,W,P
 39.10152-20.71844 32.72264 0.000000                         1110
# Lorentzian parameters - X,Xe/Xs,Y,Ye
 2.630812 0.000000 0.000000 0.000000                         1000
### phase #2SrCeO3
# Cell parameters - a,b,c,alpha,beta,gamma
 6.148000 8.586000 6.010000 90.00000 90.00000 90.00000       000000
# Gaussian parameters - U,V,W,P
 39.10152-20.71844 32.72264 0.000000                         0000
# Lorentzian parameters - X,Xe/Xs,Y,Ye
 2.630812 0.000000 0.000000 0.000000                         0000
```

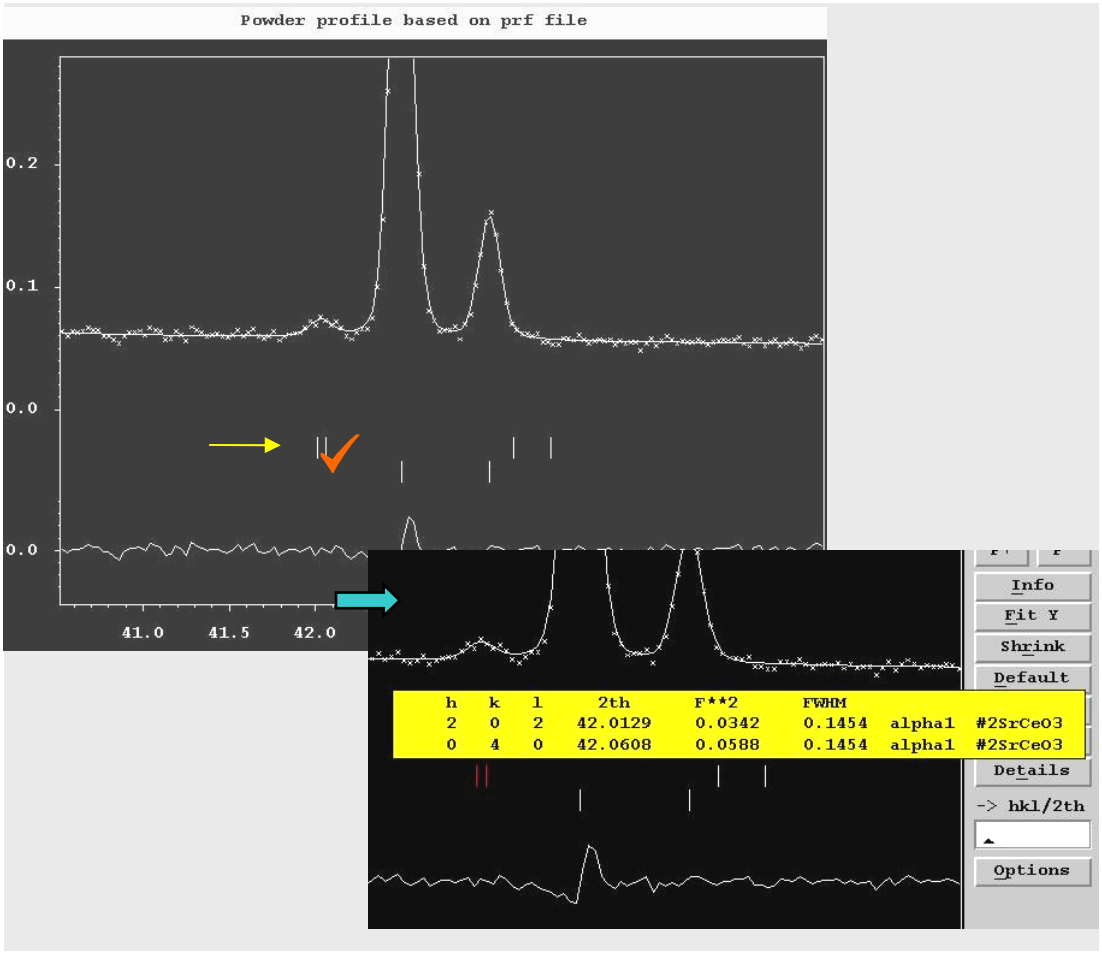
M50 after adding the new phase

```
title
lambda 1.5406 radtype 1 lpfactor 1 monangle 0.806
datcolltemp 293
------------------------------------------------------------
phase Phase#1
cell 6.120009 10.35531 3.59663 90 90 90
esdcell 0 0 0 0 0 0
spgroup Pbam 55 3
centro
lattice P
symmetry x y z
symmetry x y -z
symmetry 1/2-x 1/2+y z
symmetry 1/2-x 1/2+y -z
unitsnumb 4
chemform Sr2Ce1O4
atom Sr
atweight 87.62 atradius 3
f' -0.3528 f" 1.82
formtab -56
  38.0000  37.9460  37.7860  37.5320  37.1970  36.8020  36.3630  35.8970
  . . . .
------------------------------------------------------------
phase #2SrCeO3
cell 6.148 8.586 6.01 90 90 90
esdcell 0 0 0 0 0 0
spgroup Pnma 62 3
centro
lattice P
symmetry x y z
symmetry 1/2+x y 1/2-z
symmetry 1/2-x 1/2+y 1/2+z
symmetry -x 1/2+y -z
unitsnumb 4
chemform Sr1Ce1O3
atom Sr
atweight 87.62 atradius 3
f' -0.3396 f" 1.8517
formtab -56
  38.0000  37.9460  37.7860  37.5320  37.1970  36.8020  36.3630  35.8970
 . . . .
```

In M41, we can see that the background and shift parameters as well as the absorption correction are common for all phases. Most of the tools of *Jana2000* (*Editm40*, *EditM50*, *Powder options* etc.) are applicable only to the active phase. On the other hand, *Le Bail*, *Refine* and *Profile viewer* work for all phases together.

If we activate the new phase and look at *Powder options* we see that their values have been taken from the first phase[1]. The refinement keys, however, are checked only for the common parameters, i.e. for background parameters and the shift parameter.

After introduction of the new phase, we can execute *Tools* → *Powder* → *Make LeBail*. In the *Profile viewer* we shall see new row of Bragg positions corresponding to the new phase that exactly fits with the yet unexplained peaks. When we click the left mouse button near a Bragg position indicator, we will get an information window with details about the peaks including their phase identifier.



The relative amount of the second phase is below 2%. The refinement of its structure is not possible and the structure parameters must be fixed by the *Fixed* command. With the atom names as shown above we can simply fix *All parameters* for atoms *_b. The refinement will only change scale parameters and its influence to the structure model of the first phase will be negligible. The refined relative amounts of the phases are available in the bottom of the refinement listing.

[1] The powder parameters can be copied between phases by *Tools* → *Powder* → *Reset powder parameters*.

1.4 Modulated structure from single crystal

In this chapter, we present solution of the incommensurate phase of anhydrous sodium carbonate, Na_2CO_3 [7]. Its basic crystallographic data are summarized in the following table:

Cell parameters (a,b,c,β)	a=8.920Å, b= 5.245Å, c=6.050Å, β= 101.35°
Radiation:	MoKα
Monochromator angle	6.07°
Space group of the basic structure	C2/m
q vector	(0.182,0.000,0.322)
Superspace group	C2/m(α0γ)0s
Chemical formula	Na_2CO_3

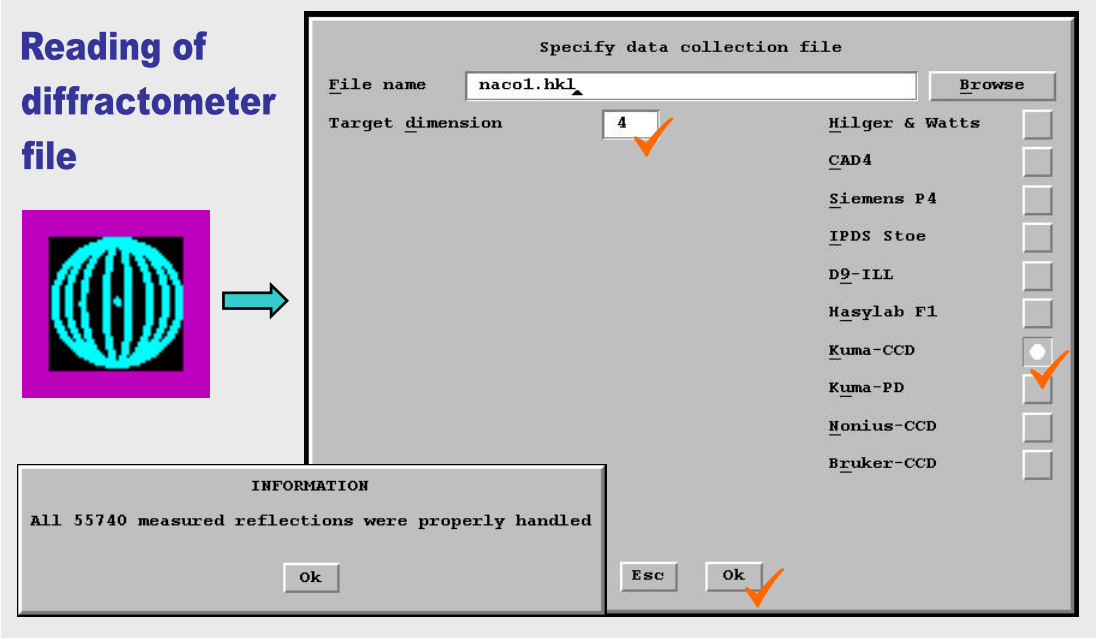
The structure was measured using KUMA diffractometer with CCD detector. The reduced diffractometer data containing satellites up to the forth order are available in the WWW page of Jana2000 as **naco1.zip**.[1]

1.4.1 Reading of data

Although Jana2000 can read directly the integrated data from KUMA,[2] we shall demonstrate several ways of reading data of a modulated structure.

1.4.1.1 Reading the diffractometer data with four integer indices

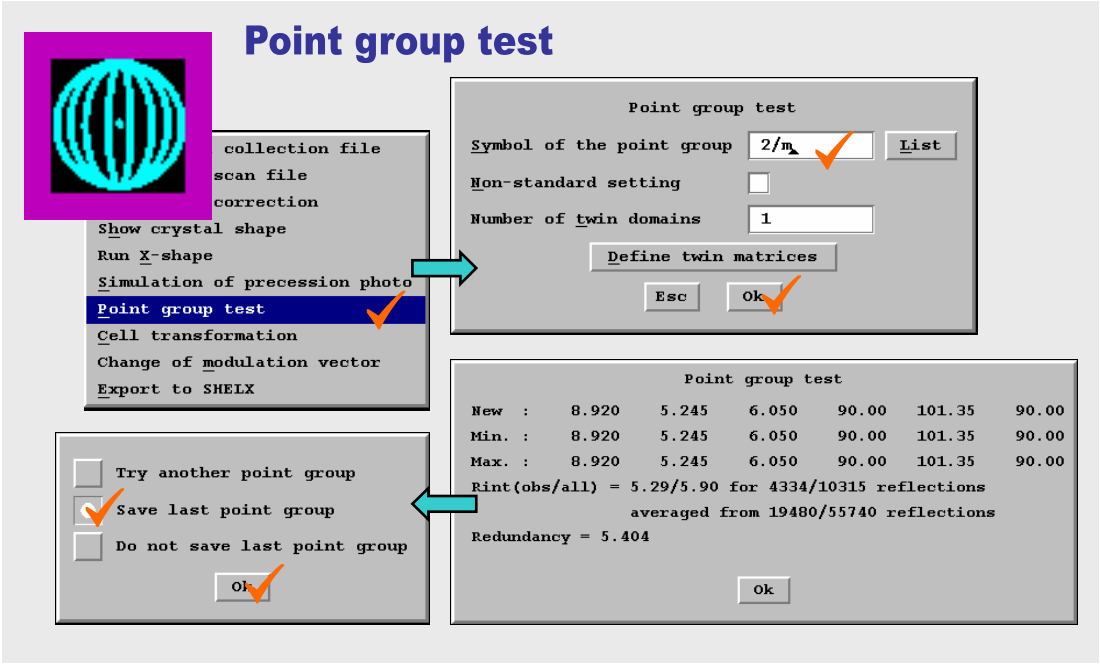
The most natural way is to import directly data produced by the diffractometer software. In our case, it is naco1.hkl file created by KUMA/Xcalibur integration software and its counterpart naco1.sum with the basic crystal information. The integration was performed using four indices and the **q** vector is available in the sum file. The data in naco1.hkl have been already corrected for LP factors but not for absorption. This could be done by *Jana2000* using the direction cosines recorded to the file but the absorption is negligible in our case.



[1] http://www-xray.fzu.cz/jana/Jana2000/manual/examples/naco1.zip

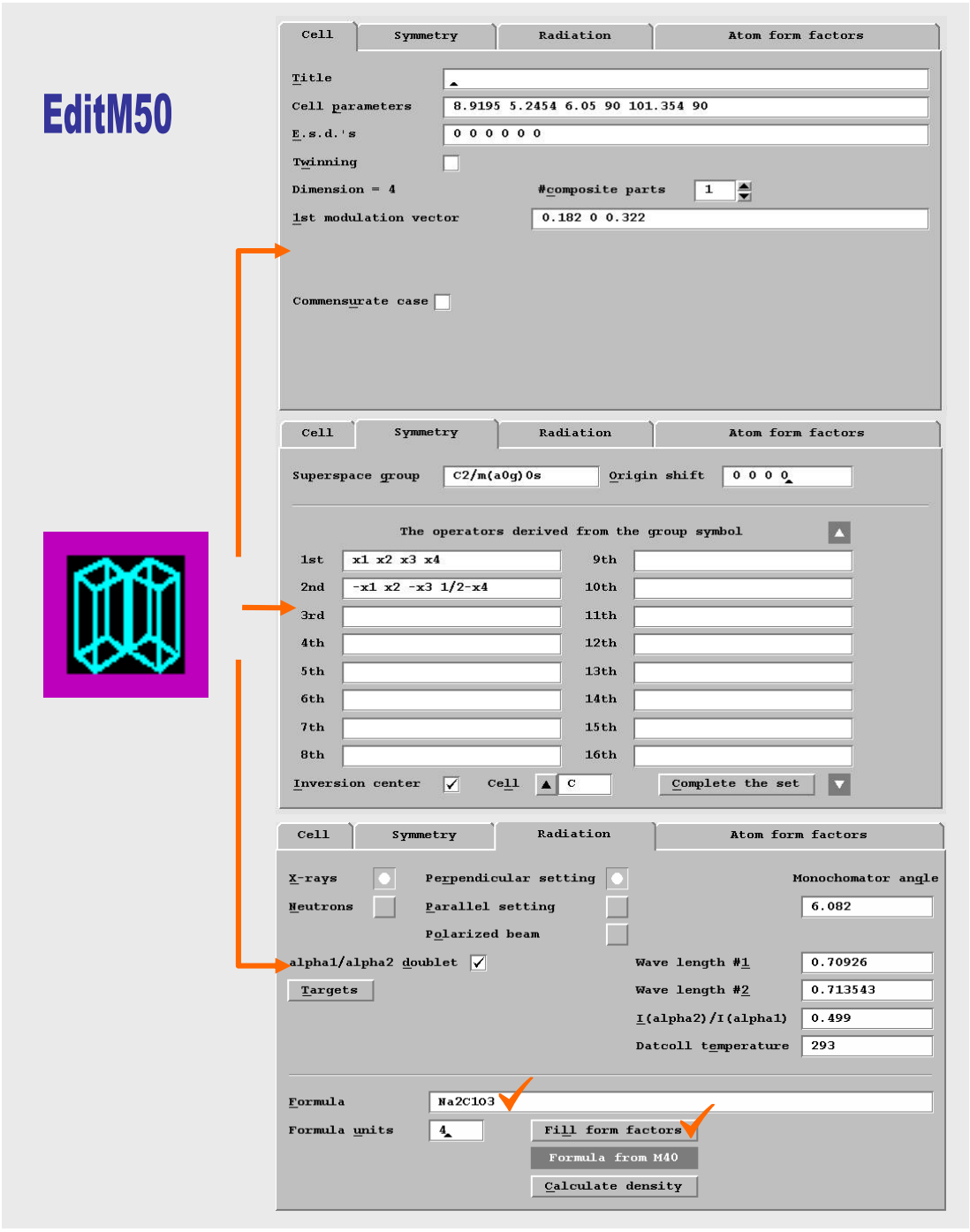
[2] Currently Xcalibur

In the same program *Datred* we run the *Point group test*. It not only verifies the point group symmetry but also rounds the celll parameters according to the saved point group.

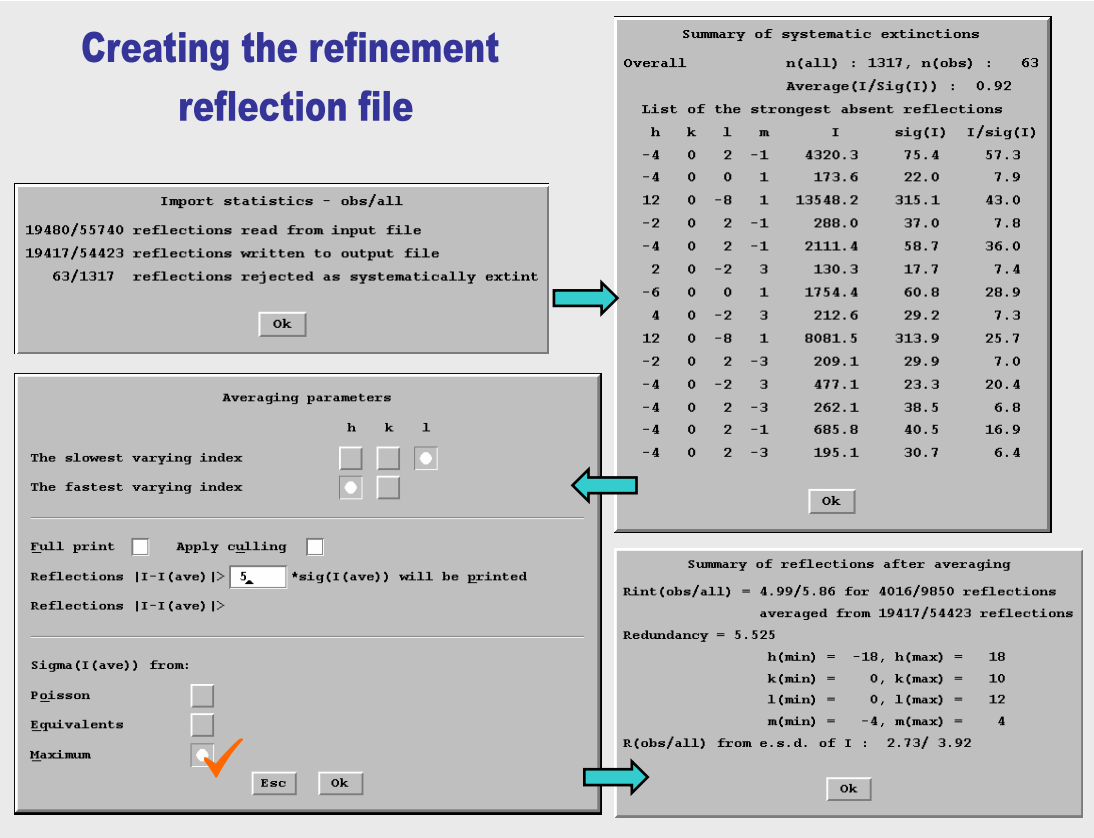


In the next step, we edit the basic crystal information by *EditM50*. In the *Cell* subwindow, the *Dimension* option is set to four and it cannot be changed, as any change would be incompatible with the imported data[1]. Values of the **q** vector components indicate that an incommensurate approach can be used. The formula and number of formula units must be entered as close as possible to the correct cell content in order to get a solution from *SIR97*.

[1] *Dimension* can only be changed when M94 and M95 files do not exist.



After quitting *EditM50* the refinement reflection file is created by discarding systematically extinct reflections and averaging reflections according to the given symmetry. Since the CCD data suffer by deeply underestimated sigmas we use *Maximum* option in *Averaging parameters* that compares sigmas resulting from the Poisson statistics and the ones resulting from averaging symmetrically equivalent reflections and uses the larger ones for the refinement.



The program discards several strong reflections. Normally, this would indicate an incorrect symmetry but in our case, this is caused by a weak admixture of another domain of Na_2CO_3 in the sample. The integration of CCD data is combined with local peak hunting in the predicted peak position that may cause a skip from an extinct diffraction spot of the first domain to a non-extinct peak of the second domain.

1.4.1.2 Reading reflection file with four integer indices

Very often, the input is not a diffractometer file supported by *Datred* but a reflection file processed by some data reduction program. In this paragraph, we shall use as an input a reflection file containing reduced and corrected diffraction data indexed with four indices. There is no information available in the file about direction cosines and orientation matrix. Such data can be imported by *File →Reflection file →Import file(s) from various sources*.

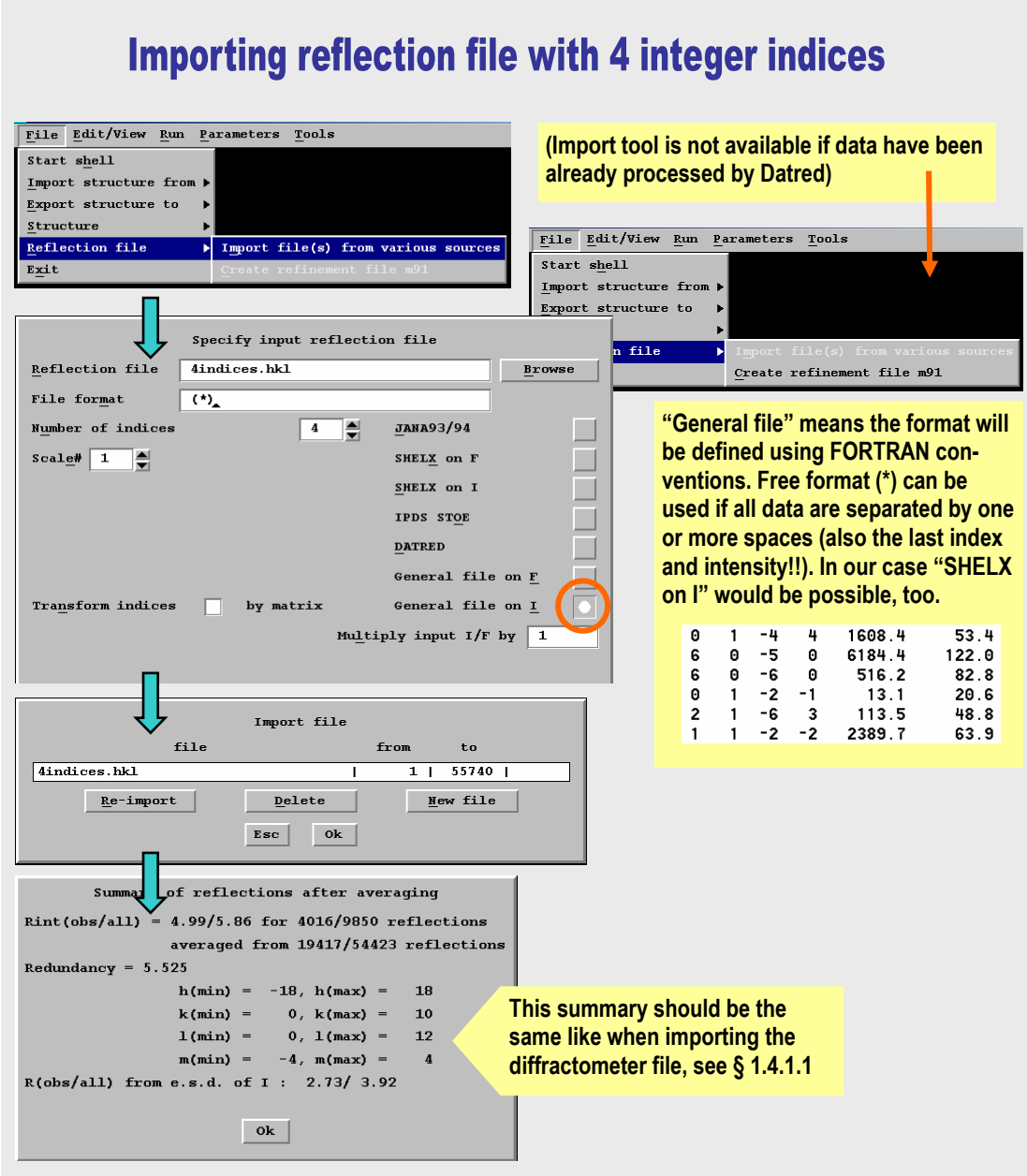
In the first step, we create a new job name[1] by *File → Open* and define the basic crystal information by *EditM50*. The dimension must be 4, the **q** vector, super space group, radiation, chemical composition and atomic form factors are the same like in § 1.4.1.1 . Then we start *File →Reflection file →Import file(s) from various sources* and select the filename 4indices.hkl (it is available in **naco1.zip**.[2]). We define its format and number of indices in the *Specify input reflection file* form. The format specification follows the conventions of FORTRAN programming language. Note that in our case number of indices is compatible with the dimension defined in *EditM50*.

[1] In the current job, the import of the reflection file is disabled, as data from diffractometer file are already present. These two kinds of input cannot be combined. Another way to enable the import tool is to create a new job name by *File → Structure → Open* and import M40, M50 but not the other basic files by *File → Structure → Copy in* tool.

[2] http://www-xray.fzu.cz/jana/Jana2000/manual/examples/naco1.zip

In the scheme below it is also shown that the import tool is not available if some data have been already imported by *Datred* because a diffractometer file cannot be combined with imported files.

After successful import of data we create the refinement reflection file M91 and continue with solution of the average structure (see § 1.4.2).

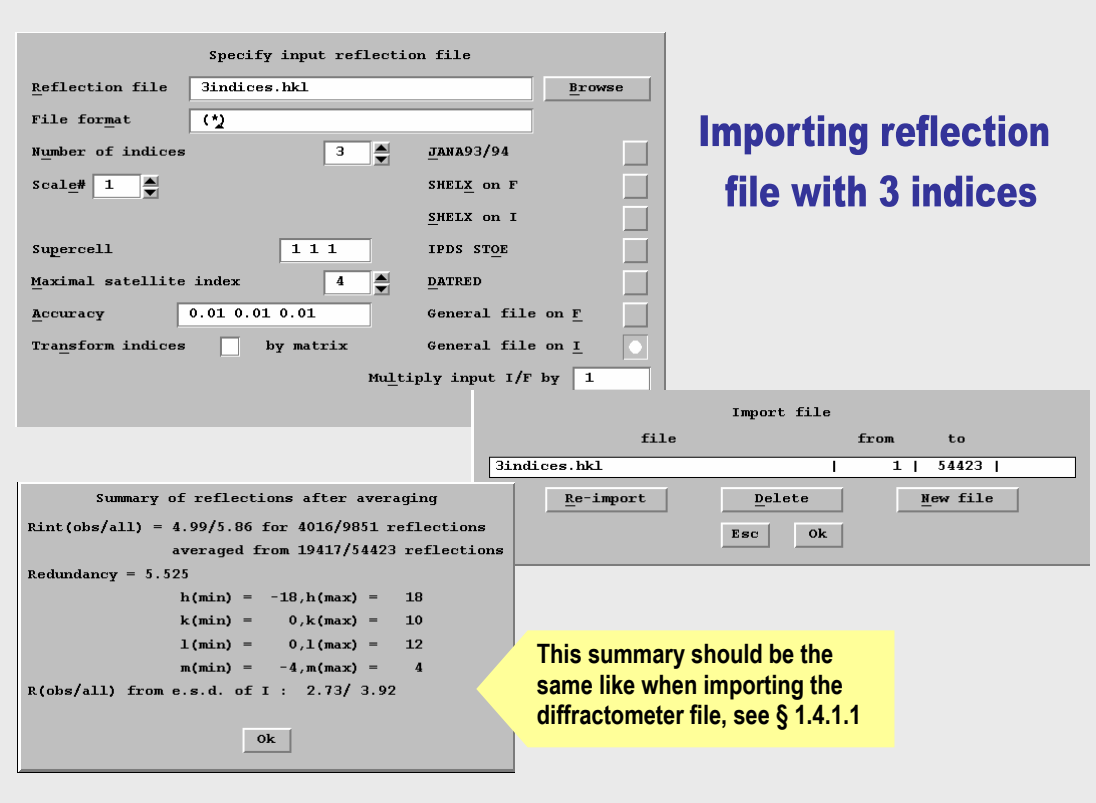


1.4.1.3 Reading reflection file with 3 real indices

In this example we suppose the same situation like in § 1.4.1.2 but we shall import reflection file indexed with three real indices (3indices.hkl available in **naco1.zip**.[1]). In this case, the import tool transforms the real indices to integer indices using information about number of dimensions and value of the **q** vector defined in *EditM50*. The *Accuracy* text box defines tolerance for the values of the real indices that do not correspond exactly to the values of the **q** vector components. The *Supercell* and *Transform indices* options enable various transformations of imported data that will be discussed elsewhere. Unlike the reading of four indices, the program

[1] http://www-xray.fzu.cz/jana/Jana2000/manual/examples/naco1.zip

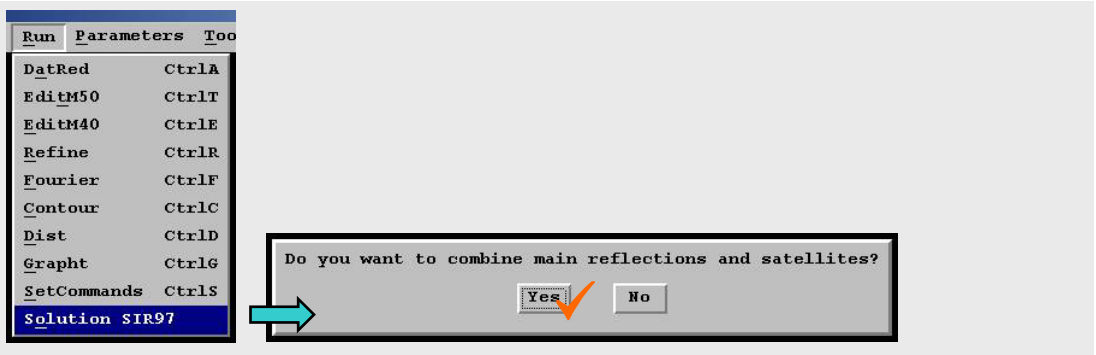
also uses the superspace symmetry to detect systematic extinctions. The extinct reflections are therefore discarded already during the import and not as usually during creation of M91.



1.4.2 Average structure

1.4.2.1 Solution by direct methods

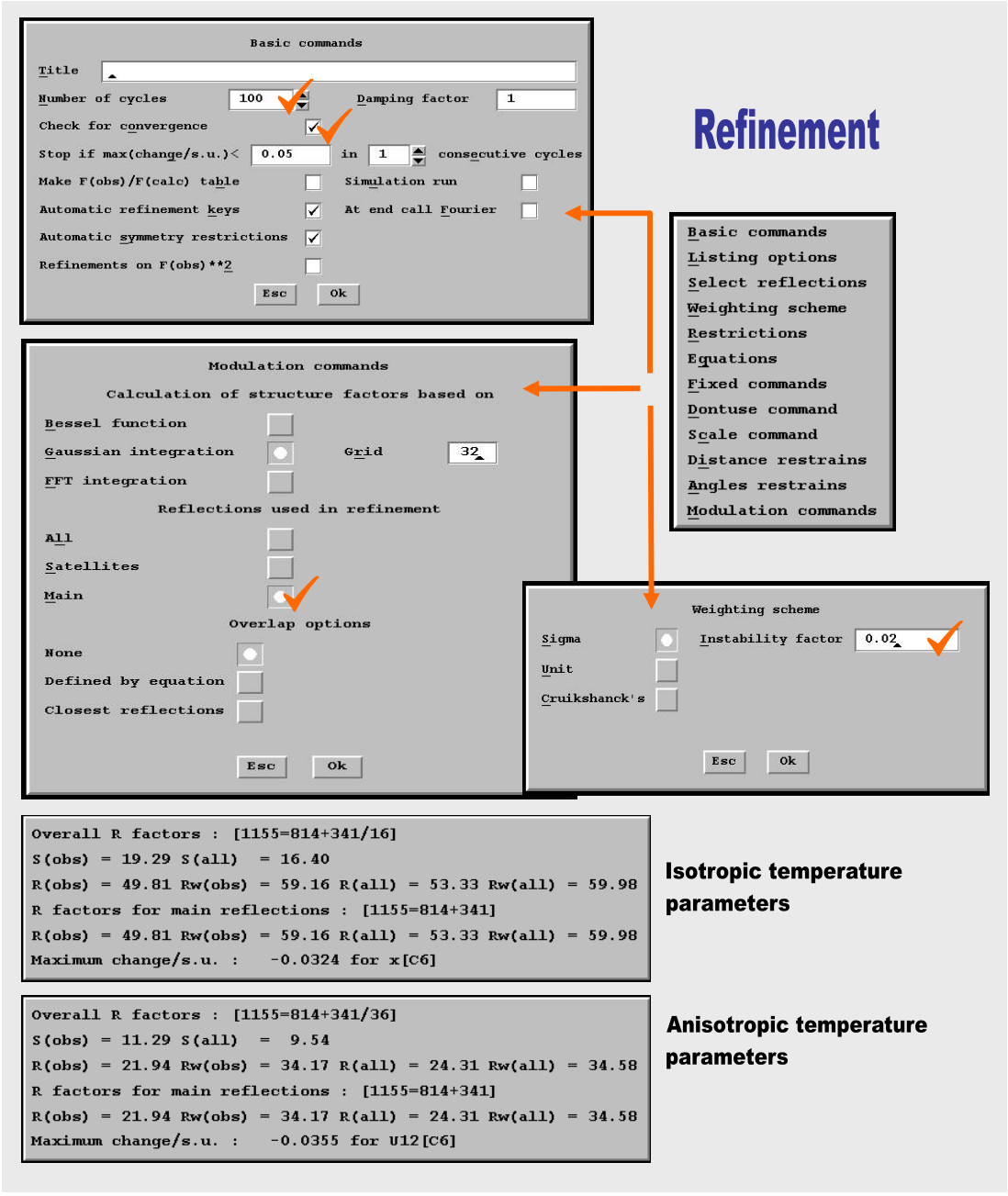
Sodium carbonate is strongly modulated and its structure determination from only main reflections is far from reality. Nevertheless, the average structure can be solved by *SIR97* if we use as an input main reflections combined with satellites. The first structure model returned by *SIR97* can be used for refinement of average structure although its R-value of 26% value is reported by *SIR97* as unsatisfactory[1].



In the next step, we shall refine the structure model from SIR97. In the refinement commands we choose only main reflections for calculation, set the instability factor to 0.02, number of refinement cycles to 100 and automatic checking of convergence.

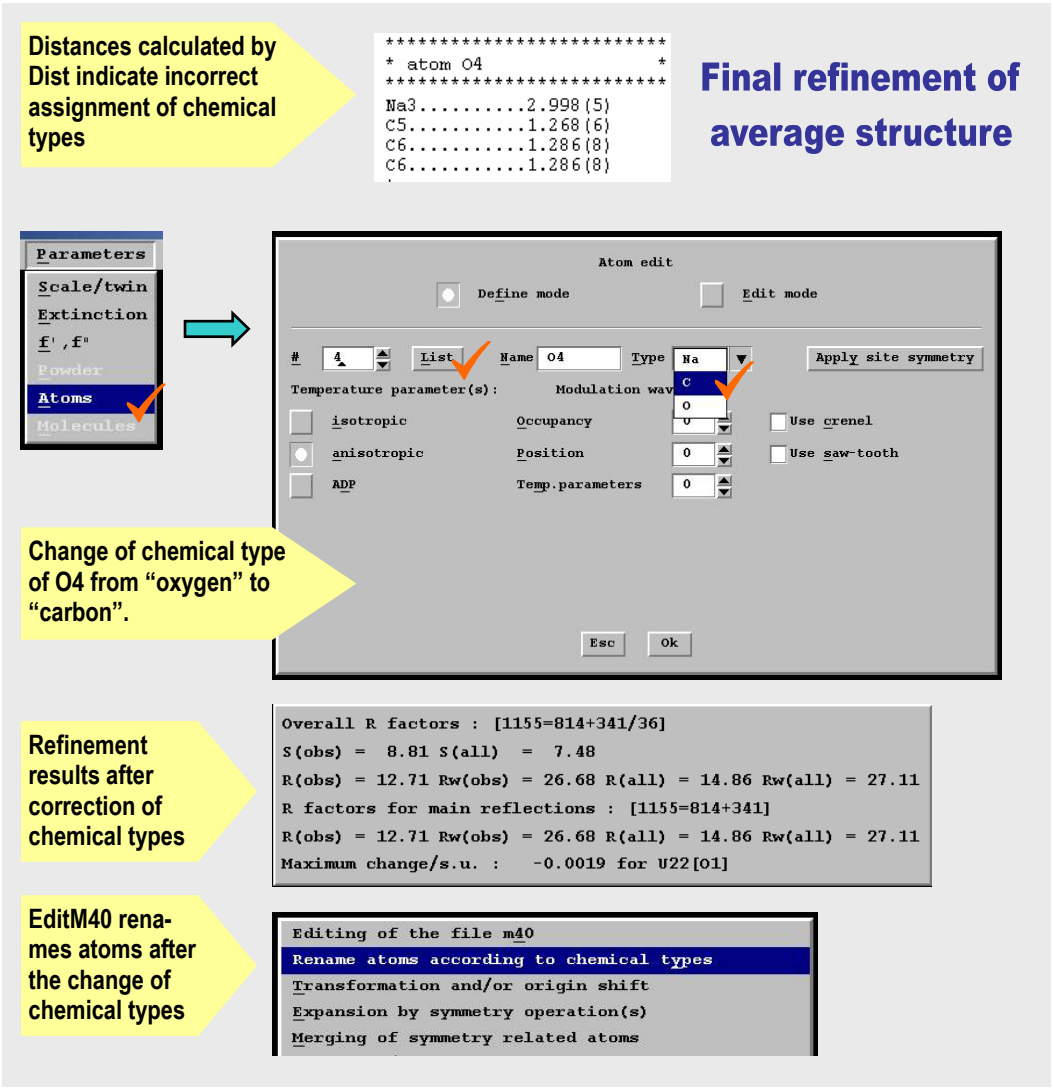
[1] Windows users should use SIR97 with care as it crashes during refinement of the second model. There is a small time delay when SIR97 reports unsatisfactory R value of the first model and asks whether to continue. The user must answer “No” during this delay. Otherwise SIR97 will proceed with another model and crash. This does not occur with UNIX version.

The refinement with isotropic ADP converges to R-value about 50% that drops down to about 22% after change to harmonic ADP.



The structure must contain CO_3 group with the typical C-O distances. It helps to verify with program *Dist* whether chemical types of carbon and oxygen have been properly assigned by *SIR97*. In our case, they have been interchanged[1]. The chemical types can be redefined by editing corresponding numbers in M40 or by *Parameters →Atoms* tool (see below). New refinement converges to R value 12%. At the end, we run *EditM40 →Rename atoms according to chemical types* to ensure the atom labels are consistent with chemical types.

[1] It may depend on the operating system. SIR97 under UNIX gives sometimes slightly different solution of the Windows version.



1.4.2.2 Creating motifs in M40

For further calculation, it is advisable that atoms neighboring in the structure are neighboring in M40, too, even if no translation or rotation symmetry is applied. This is necessary for introducing "molecules" and applying the rigid body approach to modulation displacements. It also facilitates definition of general sections. Normally the chemical fragments in M40 can be built when adding atoms one by by the *Replacing/Inserting atoms* tool of *EditM40.*. However, it is not guaranteed for M40 imported from *SIR97*.

We can see from *Edit/View→Editing of M40 file* that some atoms have their z coordinate larger or equal to one and that we need to perform a simple translation *x,y,-1+z*. This can be done in the editing program. Moreover, some atoms have negative x coordinate that can be translated into the first cell by the operation *1+x,y,z*. For this, we can use *EditM40→Transformation of atomic positions* as indicated in the next scheme.

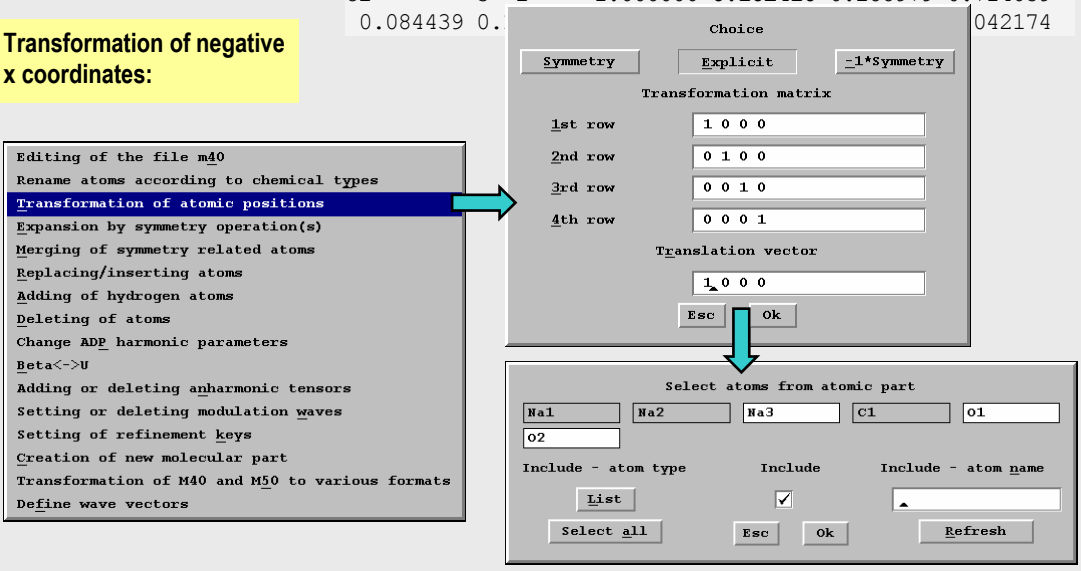
Creating Motifs in M40

1. Moving atoms to the first cell

Original M40:
The coordinates in bold should be translated to the first cell.

```
    6    0    0    0
 14.05362 0.000000 0.000000 0.000000 0.000000 0.000000
 0.000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
Na1        1  2     0.250000 0.000000 0.000000 0.500000
 0.018117 0.088773 0.016176 0.000000 0.007018 0.000000
Na2        1  2     0.250000 0.000000 0.000000 1.000000
 0.016378 0.075904 0.016003 0.000000 0.006151 0.000000
Na3        1  2     0.500000-0.328990 0.000000 0.748563
 0.020384 0.111419 0.029666 0.000000 0.008427 0.000000
C1         2  2     0.500000 0.335908 0.000000 0.750838
 0.009047 0.078580 0.009242 0.000000 0.001293 0.000000
O1         3  2     0.500000-0.211082 0.000000 1.176573
 0.015823 0.035220 0.025142 0.000000 0.011611 0.000000
O2         3  2     1.000000-0.102410 0.288979 0.714059
 0.084439 0.                                      042174
```

Transformation of negative x coordinates:



We can check with Refine that the transformation is correct.

```
Overall R factors : [1155=814+341/36]
S(obs) =  8.81 S(all)  =  7.48
R(obs) = 12.71 Rw(obs) = 26.68 R(all) = 14.86 Rw(all) = 27.11
R factors for main reflections : [1155=814+341]
R(obs) = 12.71 Rw(obs) = 26.68 R(all) = 14.86 Rw(all) = 27.11
Maximum change/s.u. :   -0.0019 for U22[O1]
```

M40 after translations:

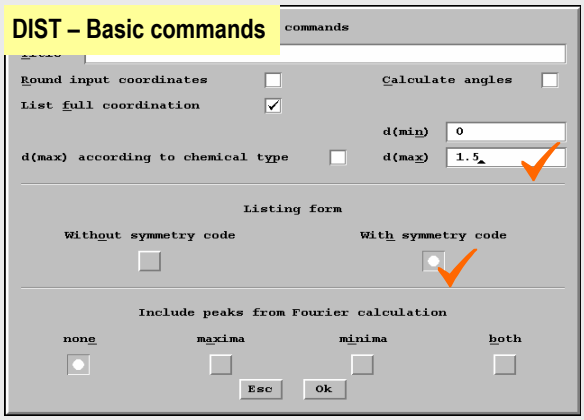
```
    6    0    0    0
 14.05363 0.000000 0.000000 0.000000 0.000000 0.000000      100000
 0.000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000      000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000      000000
Na1        1  2     0.250000 0.000000 0.000000 0.500000      000  0  0  0
 0.018117 0.088773 0.016176 0.000000 0.007018 0.000000      0000111010
Na2        1  2     0.250000 0.000000 0.000000 0.000000      000  0  0  0
 0.016378 0.075903 0.016004 0.000000 0.006151 0.000000      0000111010
Na3        1  2     0.500000 0.671010 0.000000 0.748563      000  0  0  0
 0.020384 0.111418 0.029666 0.000000 0.008427 0.000000      0101111010
C1         2  2     0.500000 0.335908 0.000000 0.750837      000  0  0  0
 0.009047 0.078579 0.009242 0.000000 0.001293 0.000000      0101111010
O1         3  2     0.500000 0.788918 0.000000 0.176573      000  0  0  0
 0.015823 0.035220 0.025141 0.000000 0.011611 0.000000      0101111010
O2         3  2     1.000000 0.897590 0.288979 0.714059      000  0  0  0
 0.084438 0.138994 0.066159 0.080112 0.053758 0.042173      0111111111
```

The oxygen atoms are part of the CO_3 group are they should be transformed to make a motif. We can use *Dist* to check which atoms should be transformed and by which symmetry operators. At this point we must emphasize that the transformation made by *EditM40→Transformation of atomic positions* transforms all atomic parameters (ADP, modulation, etc.) of the selected atoms.

Creating Motifs in M40

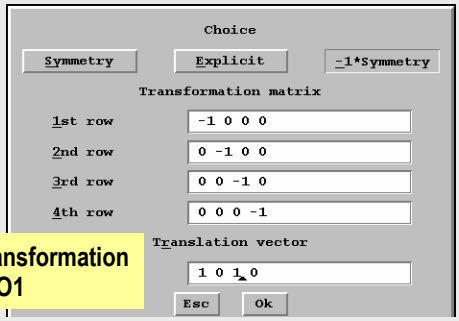
2. Creating CO3 molecule

DIST – Basic commands

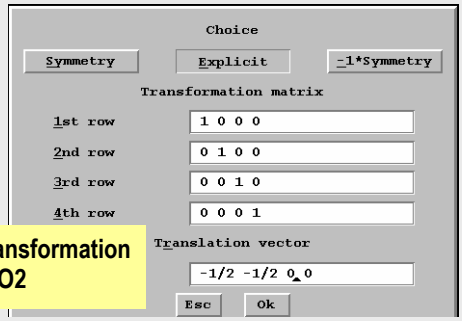


Output of Dist:
(For symmetry codes see §1.1.7)

```
Distances concerning atom C1
================================
C1-O1          1.275(4)      symmetry : 1-x,-y,1-z#s-1t1,0,1
C1-O2          1.275(5)      symmetry : -1/2+x,-1/2+y,z#c2t-1,-1,0
C1-O2          1.275(5)      symmetry : -1/2+x,1/2-y,z#s-2c2t-1,0,0
```



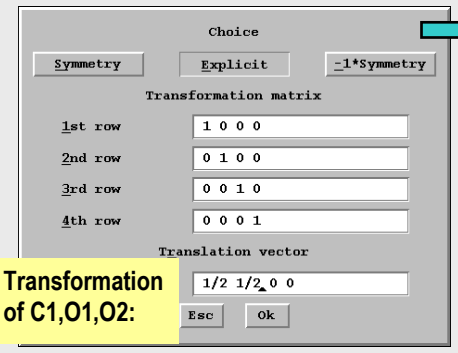
Transformation of O1



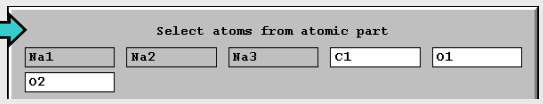
Transformation of O2

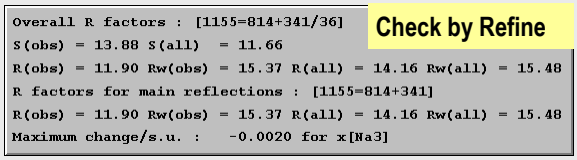
Resulting coordinates:

```
C1          2   2      0.500000 0.335908 0.000000 0.750837
 0.009047 0.078579 0.009242 0.000000 0.001293 0.000000
O1          3   2      0.500000 0.211082 0.000000 0.823427
 0.015823 0.035220 0.025141 0.000000 0.011611 0.000000
O2          3   2      1.000000 0.397590-0.211021 0.714059
 0.084438 0.138994 0.066159 0.080112 0.053758 0.042173
```



Transformation of C1,O1,O2:





Check by Refine

```
Distances concerning atom C1
================================
C1-O1          1.275(4)      symmetry : x,y,z#
C1-O2          1.275(5)      symmetry : x,y,z#
C1-O2          1.275(5)      symmetry : x,1-y,z#s-2t0,1,0
```

Final M40

```
   6    0    0    0
 14.05363 0.000000 0.000000 0.000000 0.000000
 0.000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
Na1         1   2      0.250000 0.000000 0.000000 0.500000
 0.018117 0.088773 0.016176 0.000000 0.007018 0.000000
Na2         1   2      0.250000 0.000000 0.000000 0.000000
 0.016378 0.075903 0.016004 0.000000 0.006151 0.000000
Na3         1   2      0.500000 0.671010 0.000000 0.748563
 0.020384 0.111418 0.029666 0.000000 0.008427 0.000000
C1          2   2      0.500000 0.835908 0.500000 0.750837
 0.009047 0.078579 0.009242 0.000000 0.001293 0.000000
O1          3   2      0.500000 0.711082 0.500000 0.823427
 0.015823 0.035220 0.025141 0.000000 0.011611 0.000000
O2          3   2      1.000000 0.897590 0.288979 0.714059
 0.084438 0.138994 0.066159 0.080112 0.053758 0.042173
```

New output of Dist: All atoms of CO_3 are in the first cell

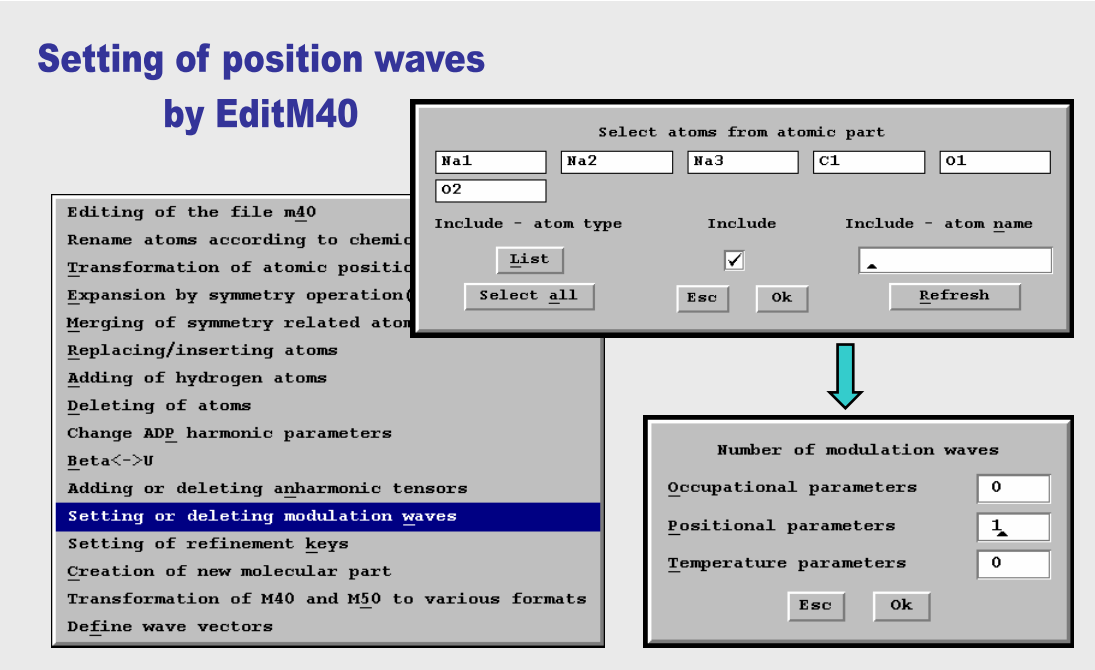
The final M40 can be downloaded from the server as **naco1_average.zip**[1]. Further in this chapter we shall use labeling consistent with this file.

1.4.3 Modulated structure

1.4.3.1 Position modulation – 1st modulation wave

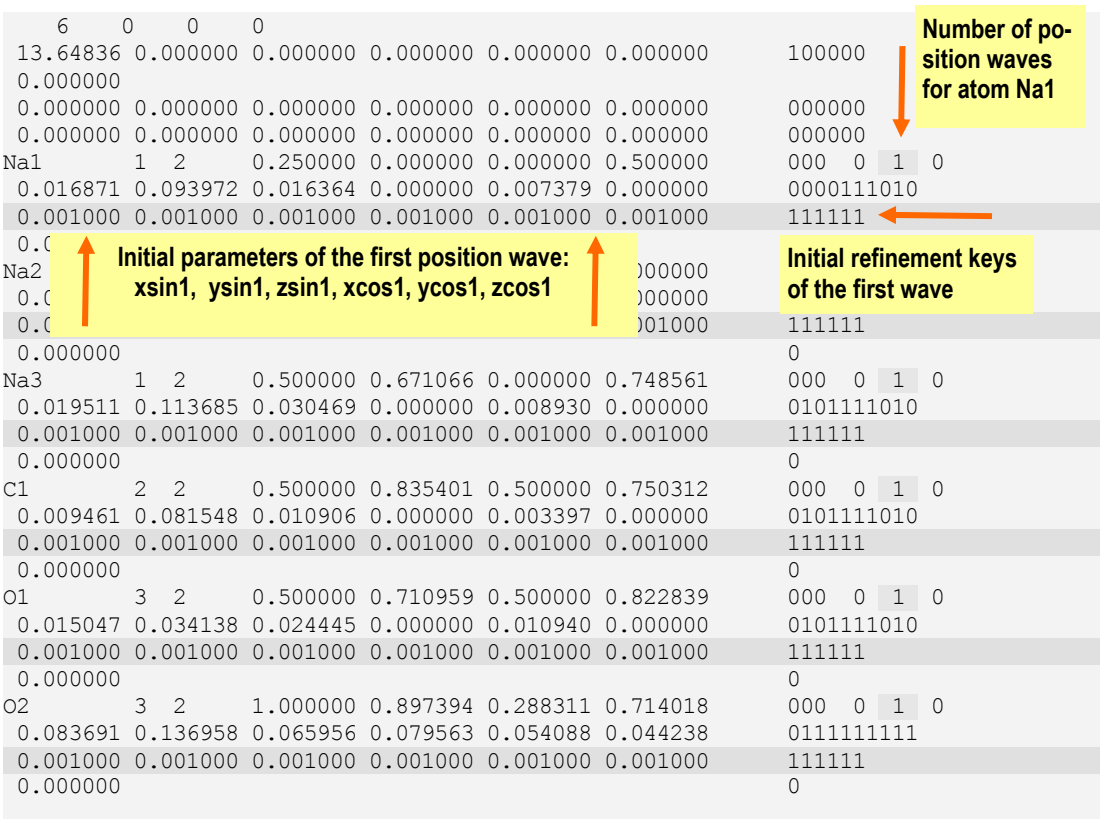
With having the average structure finished, we can start refinement of position modulation parameters. Although the modulations in Na_2CO_3 are very large, the refinement can be started from arbitrary small displacements assigned automatically by *Editm40*.

With *EditM40* we enable refinement of one position modulation wave for every atom of the structure. *EditM40* sets the modulation parameters to small positive values and it sets the corresponding refinement keys to "1". These keys are set irrespective of the symmetry restrictions following from the site symmetry. The symmetry restrictions are taken into the account by Refine if "*Automatic symmetry restrictions*" are used in the basic refinement commands. If the "*Automatic refinement keys*" option is also active, *Refine* will refine as many parameters as possible with the given symmetry.



[1] http://www-xray.fzu.cz/jana/Jana2000/manual/examples/naco1_average.zip

M40 after setting the first position modulation wave by EditM40. The symmetry restrictions have not been yet applied.

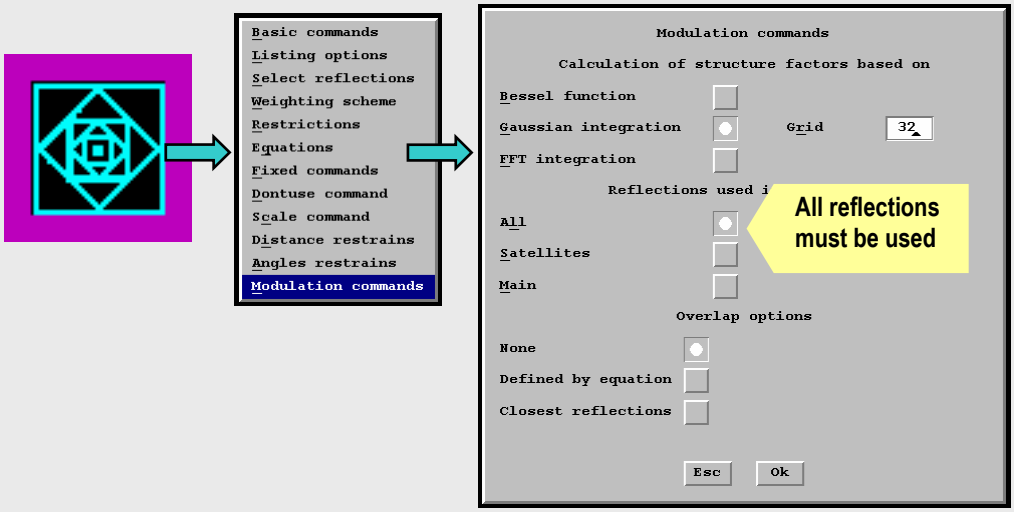


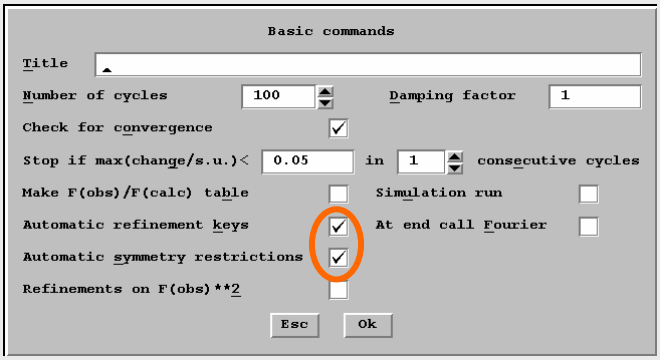

```
    6    0    0    0
 13.64836 0.000000 0.000000 0.000000 0.000000 0.000000      100000
 0.000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000      000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000      000000
Na1         1  2     0.250000 0.000000 0.000000 0.500000      000  0  1  0
 0.016871 0.093972 0.016364 0.000000 0.007379 0.000000      0000111010
 0.001000 0.001000 0.001000 0.001000 0.001000 0.001000      111111
 0.0
Na2
 0.0                                                        )00000
 0.0                                                        )00000
 0.0                                                        )01000      111111
 0.000000                                                               0
Na3         1  2     0.500000 0.671066 0.000000 0.748561      000  0  1  0
 0.019511 0.113685 0.030469 0.000000 0.008930 0.000000      0101111010
 0.001000 0.001000 0.001000 0.001000 0.001000 0.001000      111111
 0.000000                                                               0
C1          2  2     0.500000 0.835401 0.500000 0.750312      000  0  1  0
 0.009461 0.081548 0.010906 0.000000 0.003397 0.000000      0101111010
 0.001000 0.001000 0.001000 0.001000 0.001000 0.001000      111111
 0.000000                                                               0
O1          3  2     0.500000 0.710959 0.500000 0.822839      000  0  1  0
 0.015047 0.034138 0.024445 0.000000 0.010940 0.000000      0101111010
 0.001000 0.001000 0.001000 0.001000 0.001000 0.001000      111111
 0.000000                                                               0
O2          3  2     1.000000 0.897394 0.288311 0.714018      000  0  1  0
 0.083691 0.136958 0.065956 0.079563 0.054088 0.044238      0111111111
 0.001000 0.001000 0.001000 0.001000 0.001000 0.001000      111111
 0.000000                                                               0
```

M40 immediately after start of the refinement with automatic symmetry restrictions applied.

```
    6    0    0    0
 13.64818 0.000000 0.000000 0.000000 0.000000 0.000000      100000
 0.000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000      000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000      000000
Na1         1  2     0.250000 0.000000 0.000000 0.500000      000  0  1  0
 0.016871 0.093955 0.016364 0.000000 0.007379 0.000000      0000111010
 0.000000 0.001000 0.000000 0.000000 0.000000 0.000000      010000
 0.000000                                                               0
Na2         1  2     0.250000 0.000000 0.000000 0.000000      000  0  1  0
 0.016010 0.072379 0.016201 0.000000 0.006200 0.000000      0000111010
 0.000000 0.001000 0.000000 0.000000 0.000000 0.000000      010000
 0.000000                                                               0
Na3         1  2     0.500000 0.671066 0.000000 0.748561      000  0  1  0
 0.019511 0.113650 0.030469 0.000000 0.008930 0.000000      0101111010
 0.000000 0.001000 0.000000 0.000000 0.001000 0.000000      010010
 0.000000                                                               0
C1          2  2     0.500000 0.835401 0.500000 0.750312      000  0  1  0
 0.009461 0.081515 0.010907 0.000000 0.003398 0.000000      0101111010
 0.000000 0.001000 0.000000 0.000000 0.001000 0.000000      010010
 0.000000                                                               0
O1          3  2     0.500000 0.710959 0.500000 0.822839      000  0  1  0
 0.015046 0.034112 0.024444 0.000000 0.010939 0.000000      0101111010
 0.000000 0.001000 0.000000 0.000000 0.001000 0.000000      010010
 0.000000                                                               0
O2          3  2     1.000000 0.897394 0.288312 0.714018      000  0  1  0
 0.083601 0.136914 0.065915 0.079503 0.054026 0.044196      0111111111
 0.001000 0.001000 0.001000 0.001000 0.001000 0.001000      111111
 0.000000                                                               0
```

Refinement of the first position modulation wave.





Using of Automatic refinement keys and symmetry restrictions is recommended.

R factors after refinement of the first position modulation wave

number of observed reflections

number of unobserved reflections

number of reflections used in refinement

number of refined parameters

number of main reflections

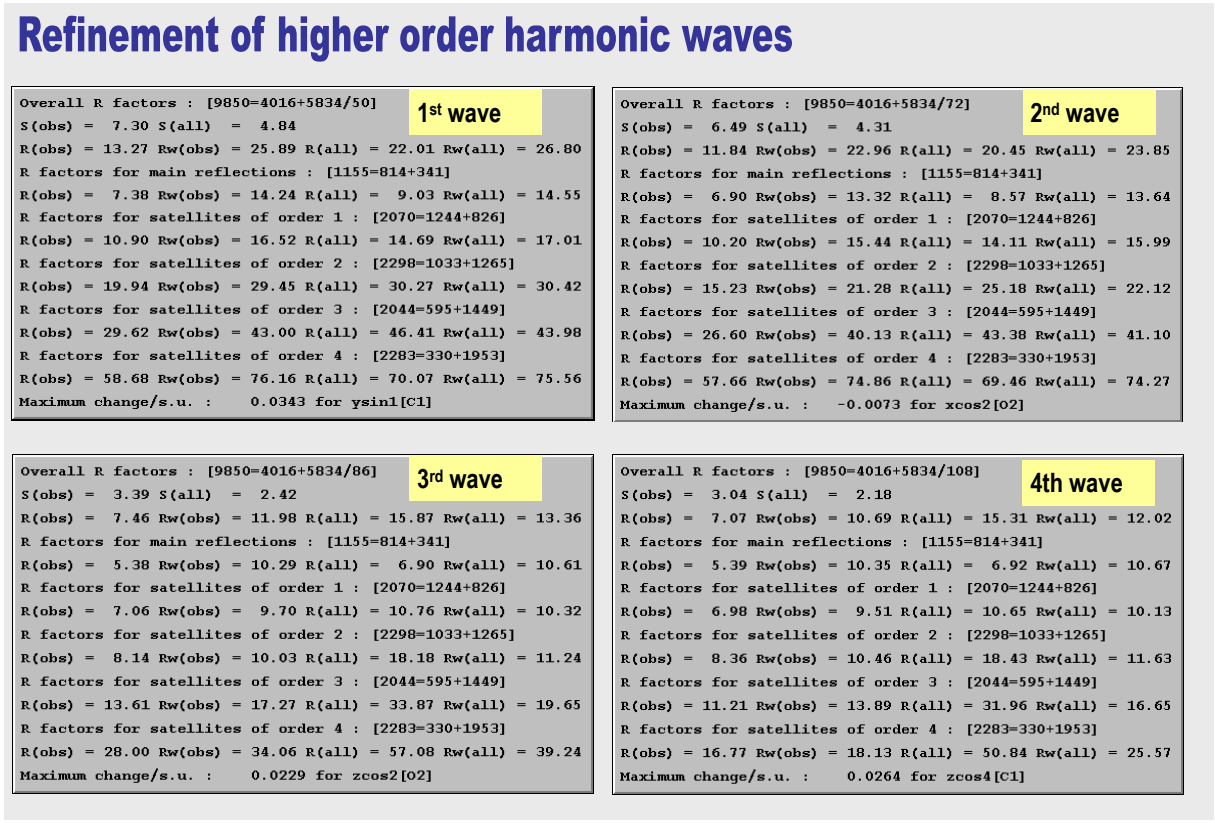
number of 1st order satellites

```
Overall R factors : [9850=4016+5834/50]
S(obs) =  7.30 S(all)  =  4.84
R(obs) = 13.27 Rw(obs) = 25.89 R(all) = 22.01 Rw(all) = 26.80
R factors for main reflections : [1155=814+341]
R(obs) =  7.38 Rw(obs) = 14.24 R(all) =  9.03 Rw(all) = 14.55
R factors for satellites of order 1 : [2070=1244+826]
R(obs) = 10.90 Rw(obs) = 16.52 R(all) = 14.69 Rw(all) = 17.01
R factors for satellites of order 2 : [2298=1033+1265]
R(obs) = 19.94 Rw(obs) = 29.45 R(all) = 30.27 Rw(all) = 30.42
R factors for satellites of order 3 : [2044=595+1449]
R(obs) = 29.62 Rw(obs) = 43.00 R(all) = 46.41 Rw(all) = 43.98
R factors for satellites of order 4 : [2283=330+1953]
R(obs) = 58.68 Rw(obs) = 76.16 R(all) = 70.07 Rw(all) = 75.56
Maximum change/s.u. :    0.0343 for ysin1[C1]
```

The first modulation wave improves significantly fit of main reflections. The first satellites are described well, too, but the others not.

1.4.3.2 Position modulation – higher order harmonic waves

Using the same tools like in the previous paragraph, we can add and refine another position modulation waves.



1.4.3.3 Visualization of atomic domains in Contour plot

An "atom" in the superspace description forms so called atomic domain, which follows a curve. This curve (modulation function) can be described by a periodic function characterized by set of refinable parameters. Using program *Fourier* in *Jana2000* we can calculate four-dimensional electron density map. With *Contour* two-dimensional sections through the map can be visualized.

A two-dimensional section through an atomic domain of atom *M(x1,x2,x3,x4)*, where *x1,x2,x3* are coordinates of M in the basic structure[1], comprises the axis $\mathbf{A_4}$ and one axis $\mathbf{A_i}$ from $\mathbf{A_1,A_2,A_3}$. The other coordinates are fixed. The basic coordinate x_i must be within the choosen interval of $\mathbf{A_i}$.

In the following scheme, we shall visualize the atomic domain of the most sharply modulated atom in Na_2CO_3, Na2. No general section can be calculated for this kind of maps so that the Fourier map must be already calculated in the desired orientation. For plotting of the remaining sections *x1-x4* and *x3-x4* we can take advantage of the option *Refresh scope* in the Fourier options that updates *scope* textbox according to the order of the map axes. In another scheme, we shall see the resulting atomic domain looks discontinuously. This is because of very sharp modulation in the *x2-x4* plane so that a single section in a different orientation does not comprise the whole domain. To get a continuous domain the map must be recalculated with non-zero interval along *x1* and *x3* and summed along these axes.

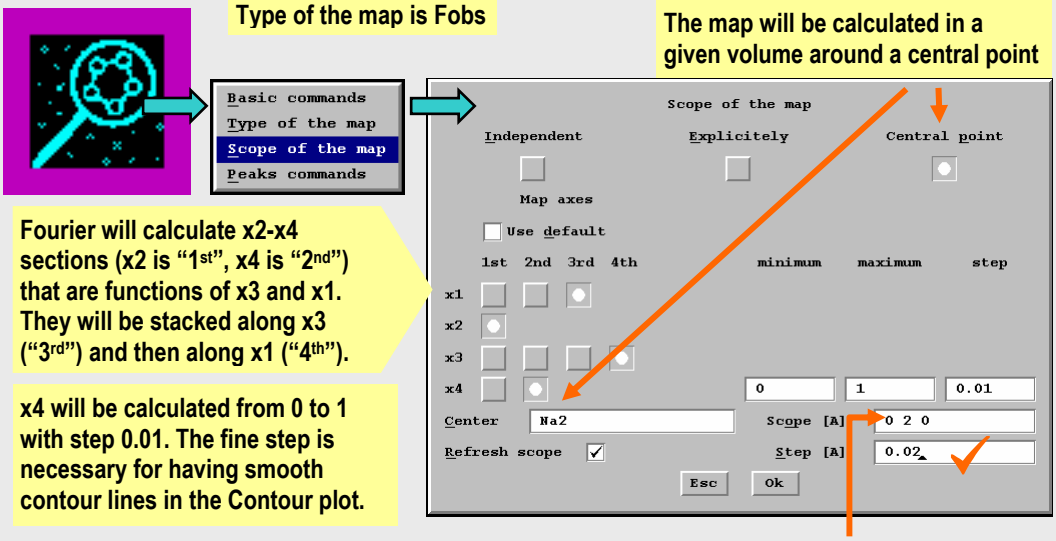
[1] The coordinates of the basic structure are given in M40. They may be very similar to the ones in the average structure but they are not necessarily the same as they do not correspond to any configuration in the real space. An average structure becomes a basic structure when we start refinement of modulation parameters.

Before calculation of Fourier map at least the zero refinement cycle must be executed.

Atomic domain of Na2

Type of the map is Fobs

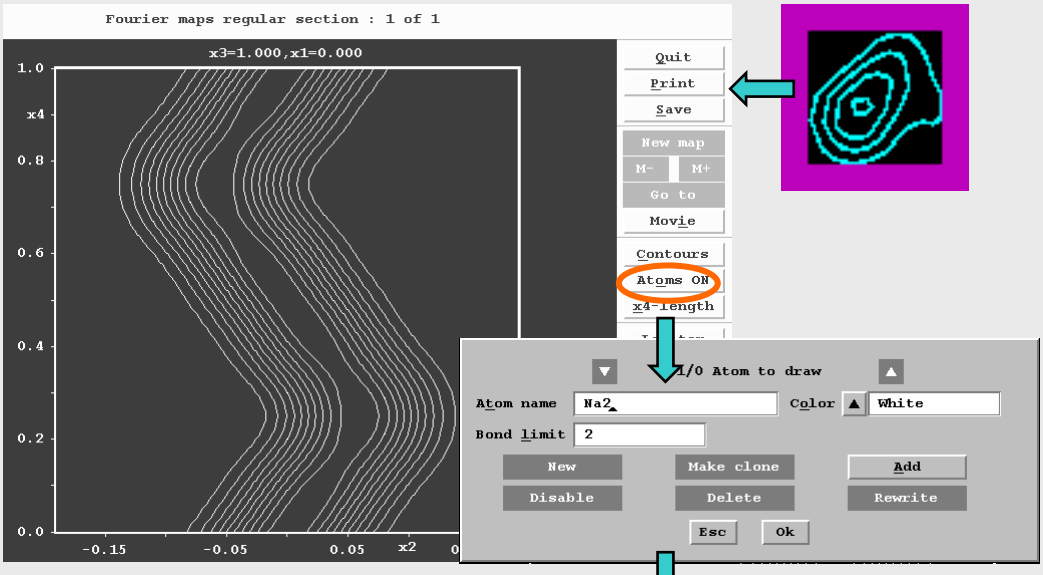
The map will be calculated in a given volume around a central point



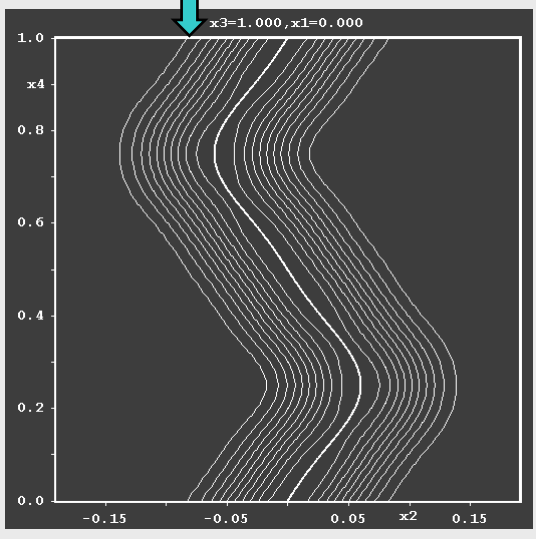
Fourier will calculate x2-x4 sections (x2 is "1st", x4 is "2nd") that are functions of x3 and x1. They will be stacked along x3 ("3rd") and then along x1 ("4th").

x4 will be calculated from 0 to 1 with step 0.01. The fine step is necessary for having smooth contour lines in the Contour plot.

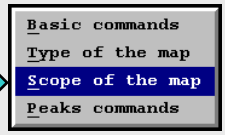
The map will be calculated for x1, x2, x3 in intervals corresponding to the volume $<x1_c-0,x1_c+0>,<x2_c-1Å,x2_c+1Å>,<x3_c-0,x3_c+0>$ around the central point $(x1_c,x2_c,x3_c)$ = position of Na2 in the basic structure, with step of 0.1Å.

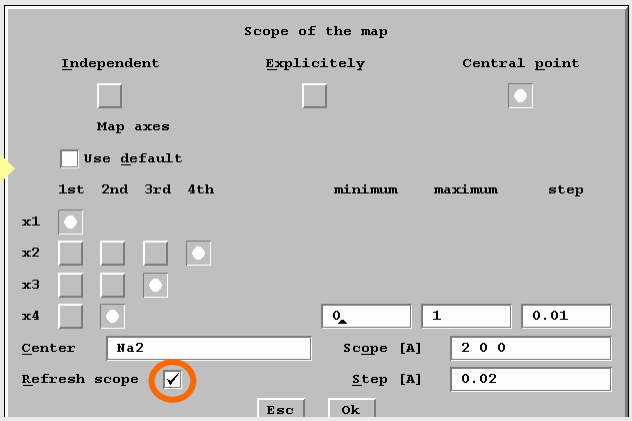


Section x2-x4 through the atomic domain of Na2. The values of x3 and x1 are fixed at the position of Na2 in the basic structure as well as the central value of x2.



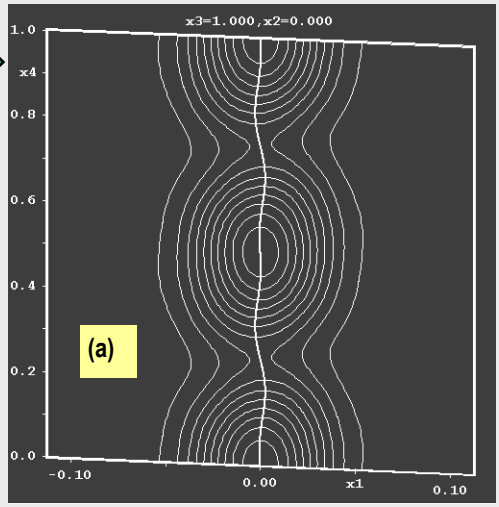
Summation of sections

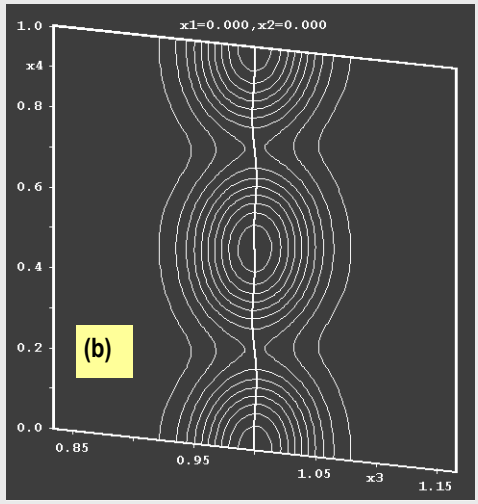




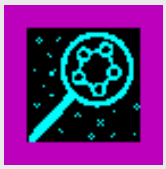
Fourier will calculate x1-x4 sections that are functions of x3 and x2. They will be stacked along x3 and then along x2.

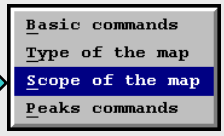
The x1,x2,x3 coordinates will be calculated in intervals corresponding to the volume <x1c-1Å,x1c+1Å>,<x2c-0,x2c+0>, <x3c-0,x3c+0> around the central point (x1c,x2c,x3c) with step of 0.1Å.

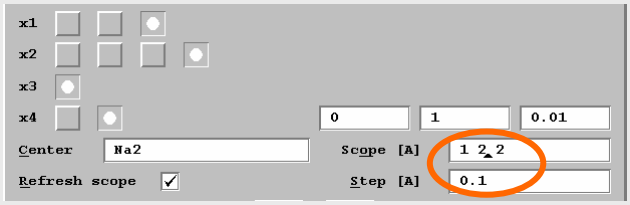




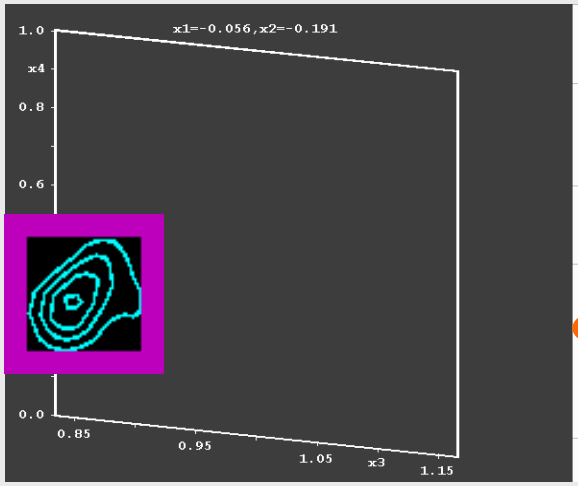
Section x1-x4 (a) and x3-x4 (b) through the atomic domain of Na2. The discontinuous character of these sections can be removed by using summation.

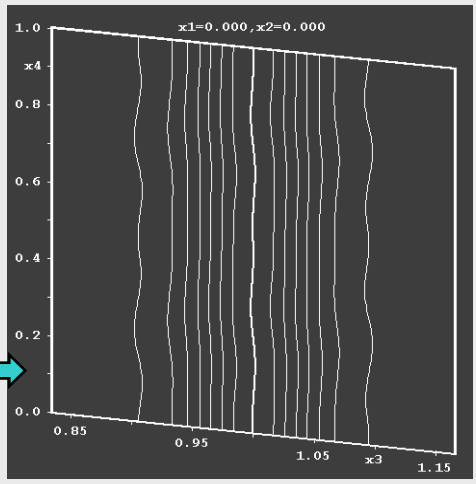






The map will be calculated for x1, x2, x3 in intervals corresponding to volume <$x1_c$-0.4Å, $x1_c$+0.4Å>, <$x2_c$-1Å, $x2_c$+1Å>, <$x3_c$-0.4Å, $x3_c$+0.4Å> around the central point ($x1_c$,$x2_c$,$x3_c$) with step of 0.1Å.





Fourier calculated many x2-x4 sections that depend on x1 and x3. This plot shows the first x2-x4 section for x1 = x1c-0.4Å and x3 = x3c-0.4Å.

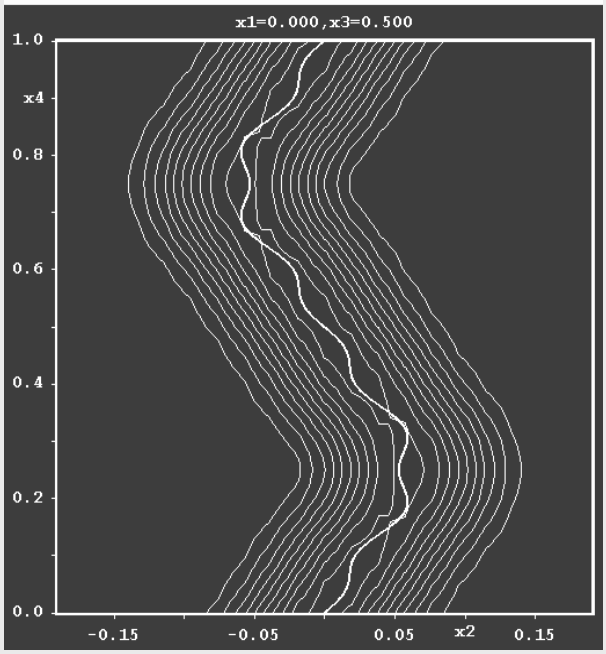
The x2-x4 sections after summation show continuous atomic domain of Na2.

1.4.3.4 Justification of used modulation parameters

The plotting of atomic domains together with refined modulation functions shown in the previous paragraph is very important for justification of the structure model. The modulation function must coincide with the atomic domain in the Fourier map. It must not be overestimated, i.e. it should describe the domain, but not marginal effects and noise.

In the case of Na_2CO_3, we can add the 5^{th} and the 6^{th} position modulation wave without a significant impact to the shape of the refined function. However, if we add the 7^{th} and 8^{th} modulation wave that are in contradiction with the satellite order known from the experiment the modulation function becomes wavy. From the x2-x4 section we can immediately say that the number of used modulation waves has no justification.

The section x2-x4 through the atomic domain of Na2 with position modulation function refined with eight harmonic waves. The shape of modulation function indicates excessive number of modulation waves.

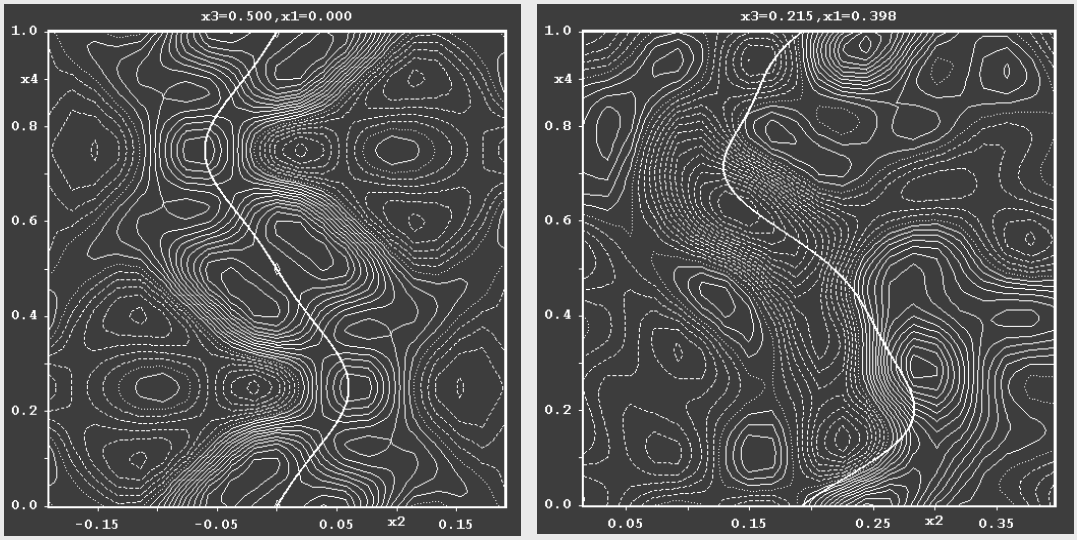


Another important check is plotting of A_3-$x4$ sections[1] based on the difference Fourier map. In the example below, we see that there are relatively strong[2] difference maxima and minima along the modulation function about $1e^{-}A^{-3}$ that are not explained by the current structure model.

[1] A_3 is x1, x2 or x3

[2] The local density can be investigated with Locator or we press Contour button to se the size of the contour step. If the plot is of summed sections, the local minima and maxima are summed, too, so that their absolute value may be misleading.

The x2-x4 section through the difference Fourier map shows the atomic domain of Na2 (a) and O2 (b). The contour step is 0.1 e-A-3 for both positive and negative local extremes.



(a) Na2 **(b) O2**

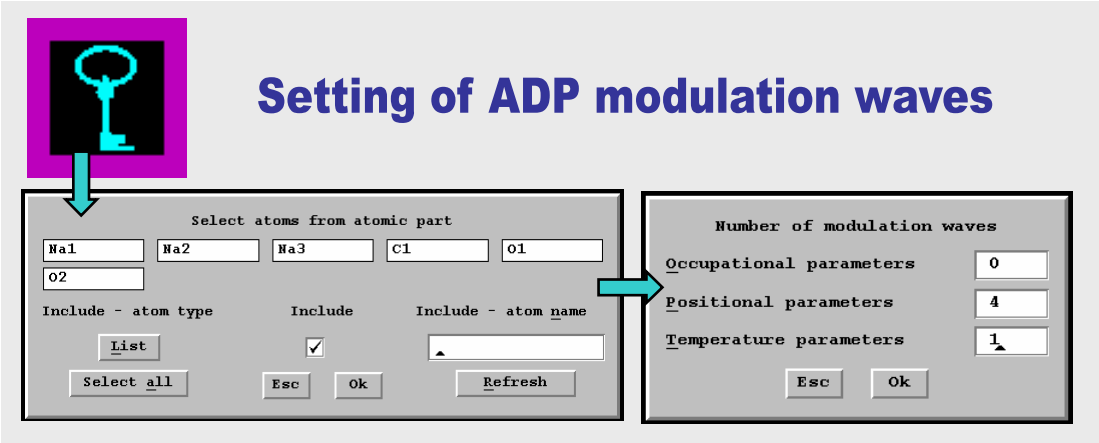
1.4.3.5 Modulation of harmonic ADP

Strong position modulation often induces modulation of ADP as a response to the varying environment of atoms. The missing ADP modulation is indicated in the difference maps as show in the previous paragraph.

In the next scheme, we shall first add one modulation wave to harmonic ADP of all atoms and then – after refinement - another one. Removing of ADP modulation of C1 in the next step and comparison of R-values reveals C1 has no significant ADP modulation. On the other hand, three waves seem to be reasonable for description of ADP modulation for atom O1 and O2.

Refinement of ADP modulation should be done with caution. A slight decrease in R-values does not necessarily justify ADP modulation since these parameters might also describe noise in the data. We have to consider whether the data quality is good enough for refinement of such small effect and if we have data enough for many new parameters. The difference maps for various models should be carefully compared and the ratio of refined parameters over sigma should be considered[1]. As a rule, we should refine only the essential number of ADP modulation parameters.

[1] The sigma of refined parameters is available in the refinement listing or at the end of M40 (the part without refinement keys).



File naco1.m40 after setting the first temperature modulation wave by EditM40. The symmetry restrictions have not been yet applied.

```
    6    0    0    0
 13.58931 0.000000 0.000000 0.000000 0.000000 0.000000      100000
 0.000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000      000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000      000000
Na1       1  2     0.250000 0.000000 0.000000 0.500000      000  0  4  1
 0.018432 0.014954 0.016384 0.000000 0.007169 0.000000      0000111010
 0.000000 0.062463 0.000000 0.000000 0.000000 0.000000      010000
 0.000340 0.000000-0.001983 0.000000 0.000000 0.000000      101000
 0.000000 0.004228 0.000000 0.000000 0.000000 0.000000      010000
 0.000745 0.000000-0.000282 0.000000 0.000000 0.000000      101000
 0.000387 0.000139 0.000178 0.000232 0.000263 0.000158      111111
 0.000387 0.000139 0.000178 0.000232 0.000263 0.000158      111111
 0                                                          0
Na                                                          000
 0                                                          0000
 0                                                          0100
 0                                                          1010
 0.000000-0.005139 0.000000 0.000000 0.000000 0.000000      0100
-0.001324 0.000000-0.000912 0.000000 0.000000 0.000000      101000
 0.000387 0.000139 0.000178 0.000232 0.000263 0.000158      111111
 0.000387 0.000139 0.000178 0.000232 0.000263 0.000158      111111
 0.000000                                                   0
. . . . . .
```

Number of position waves for atom Na1

Number of temperature waves for atom Na1

Initial parameters of the first temperature wave:
U11sin1, U22sin1, U33sin1, U12sin1, U13sin1, U23sin1
U11cos1, U22cos1, U33cos1, U12cos1, U13cos1, U23cos1

Initial refinement keys of the first temperature modulation wave

Refinement of temperature modulation parameters

1 wave for all atoms

```
Overall R factors : [9850=4016+5834/136]
S(obs) =  2.50 S(all)  =  1.86
R(obs) =  5.69 Rw(obs) =  8.76 R(all) = 13.88 Rw(all) = 10.25
R factors for main reflections : [1155=814+341]
R(obs) =  4.52 Rw(obs) =  8.93 R(all) =  5.96 Rw(all) =  9.25
R factors for satellites of order 1 : [2070=1244+826]
R(obs) =  5.00 Rw(obs) =  6.11 R(all) =  8.61 Rw(all) =  6.87
R factors for satellites of order 2 : [2298=1033+1265]
R(obs) =  6.64 Rw(obs) =  8.71 R(all) = 16.61 Rw(all) = 10.00
R factors for satellites of order 3 : [2044=595+1449]
R(obs) = 10.82 Rw(obs) = 13.40 R(all) = 31.17 Rw(all) = 16.10
R factors for satellites of order 4 : [2283=330+1953]
R(obs) = 16.07 Rw(obs) = 17.42 R(all) = 50.30 Rw(all) = 25.09
Maximum change/s.u. :    0.0402 for U22sin1[O2]
```

2 waves for all atoms

```
Overall R factors : [9850=4016+5834/180]
S(obs) =  2.03 S(all)  =  1.61
R(obs) =  4.42 Rw(obs) =  7.10 R(all) = 12.66 Rw(all) =  8.85
R factors for main reflections : [1155=814+341]
R(obs) =  3.62 Rw(obs) =  7.61 R(all) =  5.04 Rw(all) =  7.98
R factors for satellites of order 1 : [2070=1244+826]
R(obs) =  3.63 Rw(obs) =  4.93 R(all) =  7.25 Rw(all) =  5.80
R factors for satellites of order 2 : [2298=1033+1265]
R(obs) =  5.46 Rw(obs) =  6.80 R(all) = 15.38 Rw(all) =  8.26
R factors for satellites of order 3 : [2044=595+1449]
R(obs) =  8.60 Rw(obs) = 11.02 R(all) = 29.75 Rw(all) = 14.26
R factors for satellites of order 4 : [2283=330+1953]
R(obs) = 11.75 Rw(obs) = 12.76 R(all) = 48.51 Rw(all) = 22.53
Maximum change/s.u. :    0.0229 for zcos4[C1]
```

No temperature modulation of C1

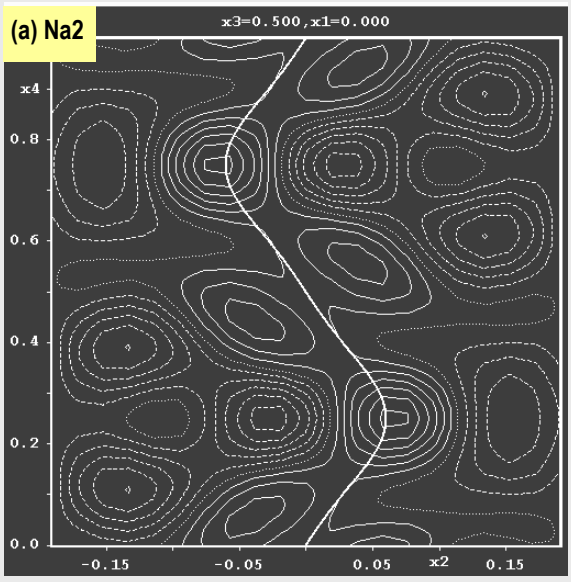
```
Overall R factors : [9850=4016+5834/168]
S(obs) =  2.04 S(all)  =  1.61
R(obs) =  4.44 Rw(obs) =  7.13 R(all) = 12.68 Rw(all) =  8.87
R factors for main reflections : [1155=814+341]
R(obs) =  3.62 Rw(obs) =  7.61 R(all) =  5.04 Rw(all) =  7.98
R factors for satellites of order 1 : [2070=1244+826]
R(obs) =  3.67 Rw(obs) =  4.95 R(all) =  7.29 Rw(all) =  5.82
R factors for satellites of order 2 : [2298=1033+1265]
R(obs) =  5.47 Rw(obs) =  6.84 R(all) = 15.38 Rw(all) =  8.29
R factors for satellites of order 3 : [2044=595+1449]
R(obs) =  8.62 Rw(obs) = 11.07 R(all) = 29.76 Rw(all) = 14.29
R factors for satellites of order 4 : [2283=330+1953]
R(obs) = 11.90 Rw(obs) = 12.90 R(all) = 48.55 Rw(all) = 22.60
Maximum change/s.u. :    0.0202 for ysin3[C1]
```

Three modulation waves for O1 and O2

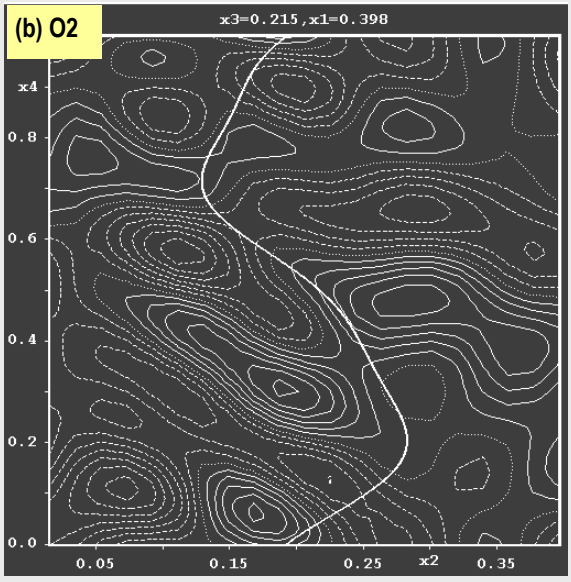
```
Overall R factors : [9850=4016+5834/184]
S(obs) =  1.99 S(all)  =  1.58
R(obs) =  4.31 Rw(obs) =  6.95 R(all) = 12.54 Rw(all) =  8.69
R factors for main reflections : [1155=814+341]
R(obs) =  3.60 Rw(obs) =  7.60 R(all) =  5.02 Rw(all) =  7.96
R factors for satellites of order 1 : [2070=1244+826]
R(obs) =  3.56 Rw(obs) =  4.84 R(all) =  7.19 Rw(all) =  5.71
R factors for satellites of order 2 : [2298=1033+1265]
R(obs) =  5.29 Rw(obs) =  6.68 R(all) = 15.19 Rw(all) =  8.15
R factors for satellites of order 3 : [2044=595+1449]
R(obs) =  8.00 Rw(obs) = 10.46 R(all) = 29.24 Rw(all) = 13.77
R factors for satellites of order 4 : [2283=330+1953]
R(obs) = 11.40 Rw(obs) = 12.29 R(all) = 48.28 Rw(all) = 22.04
Maximum change/s.u. :    0.0158 for xsin4[C1]
```

The x2-x4 section through the atomic domain of Na2 (a) and O2 (b) after refinement of temperature modulation. The contour step is 0.1 e-A-3 for both positive and negative local extremes.

(a) Na2

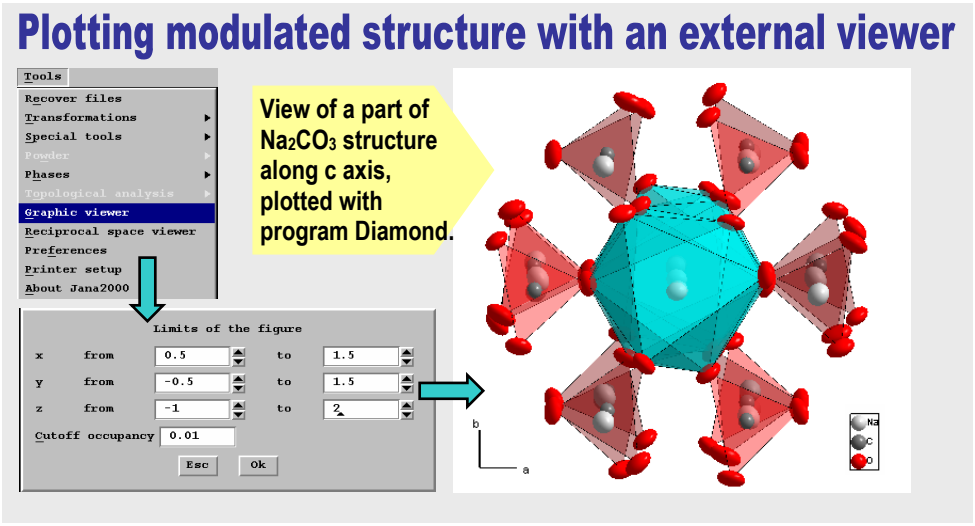


(b) O2



1.4.3.6 Interpretation of modulated structure

Jana2000 offers several tools for interpretation of modulated structures. In the real space, modulated structures are not periodic. However, if we plot a sufficiently large portion of modulated structure in three dimensions the behavior of position-modulated atoms usually becomes clear. *Jana2000* can export modulated structure into a user defined three-dimensional area as a standard structure with one large cell of symmetry P1 and call an external viewer to plot it.



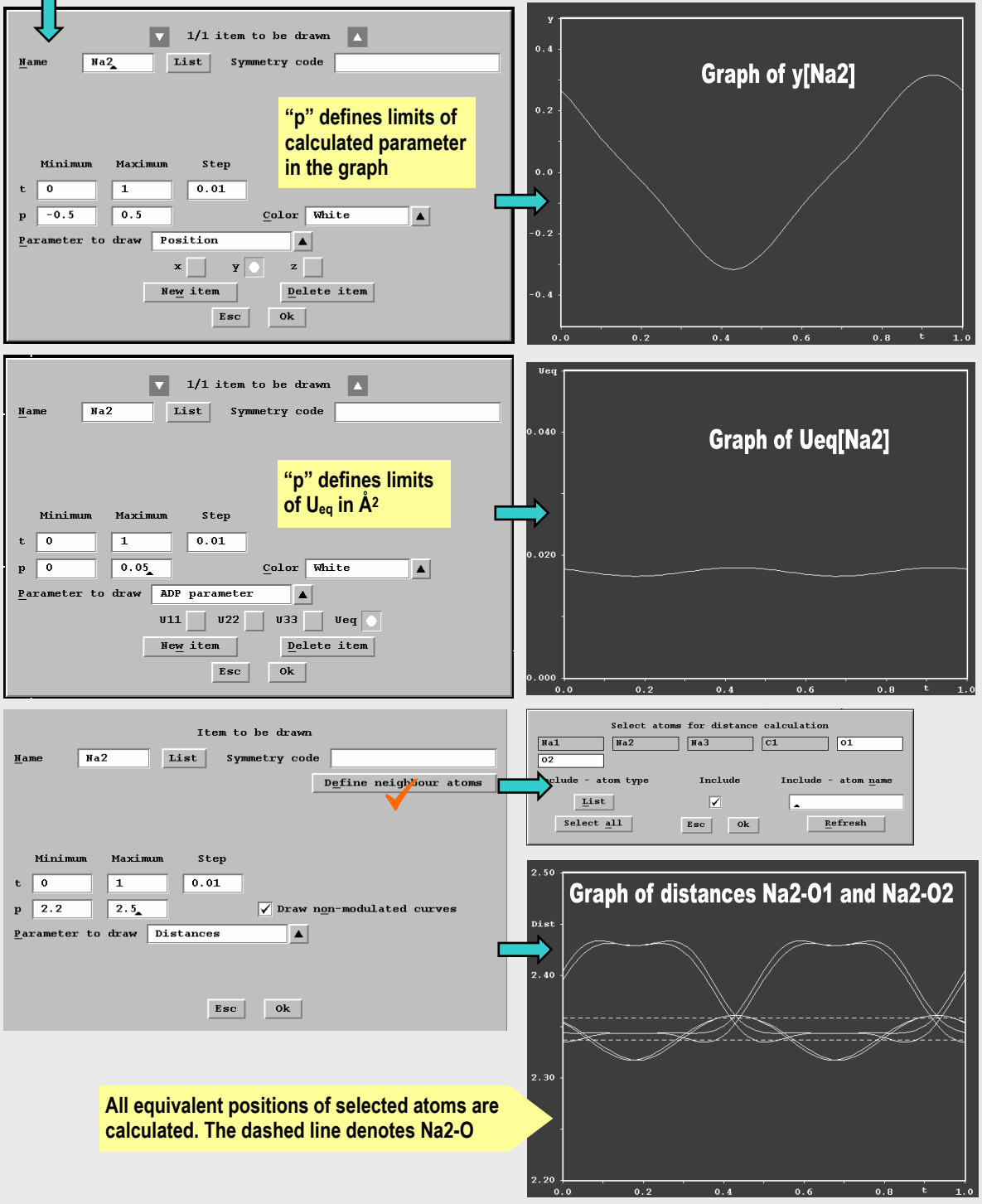
In the real space, not all configurations of the investigated structure are plotted as the expanded area is limited. *Grapht* plots refined parameters as a function of internal *t* coordinate[1]. A graph in interval of *t* <0,1) gives a complete overview of all possible configurations that occur *somewhere* in the real space. Often used plots are the ones of position parameters, interatomic distances and U_{eq}. Very useful for understanding the structure are plots of bond valence sums.

Numerical information is provided by *Dist* that calculates distances, angles and complete coordinations in modulated structure as a function of *t* coordinate. The user can define the step in *t*.

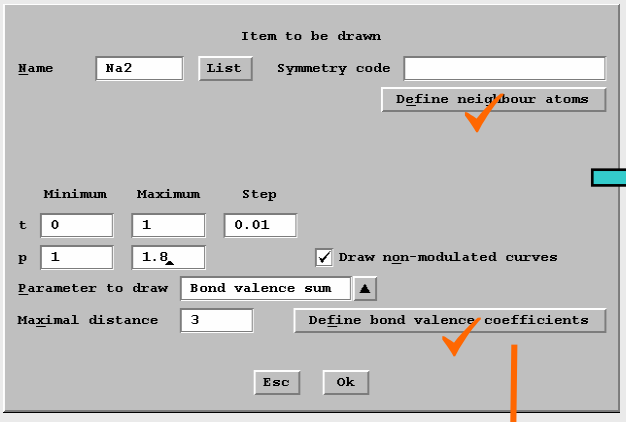
As an aid for creation of tables *Jana2000* can produce text files jobname.tb? by *Tools* → *special tools* → *tables for publications*. In these files, the semicolon stands for column delimiter and the caret symbols close the text that should be printed as a superscript. An example of conversion of file tbd into a Microsoft Word table is given in Appendix G, page 129.

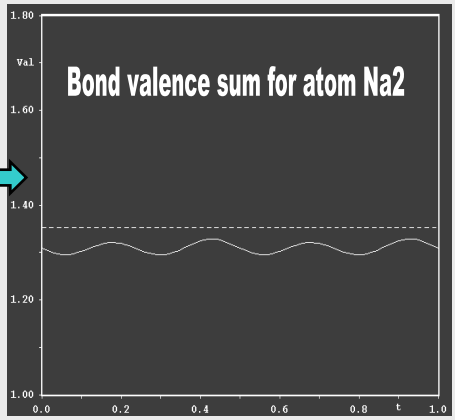
[1] *t* is projection of x4 to the A_4 axis along R_3 direction: $t = x_4 - \mathbf{q} \cdot \mathbf{r}$.

Examples of using Grapht

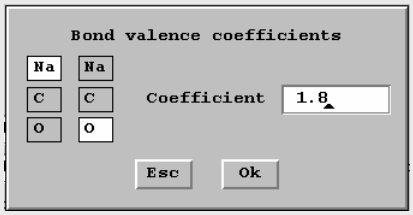


Examples of using Grapht (continued)

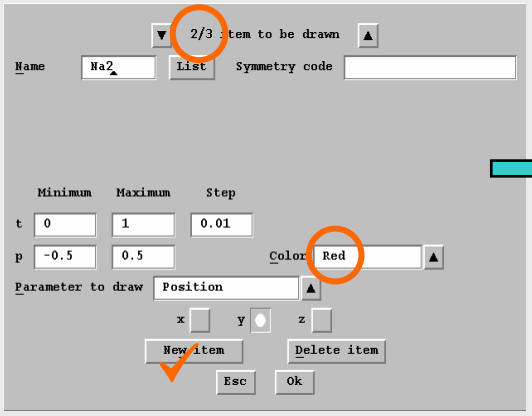


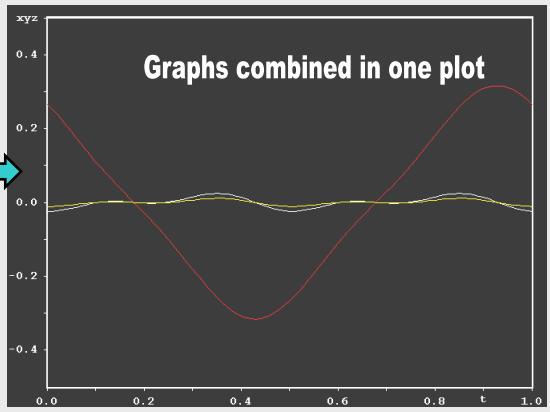


In this plot, the bond valence sum is calculated for all atoms in the 3Å neighborhood of Na2. As the Na-C and Na-Na coefficients are implicitly zero it is in fact sum of Na2-O bond valences.

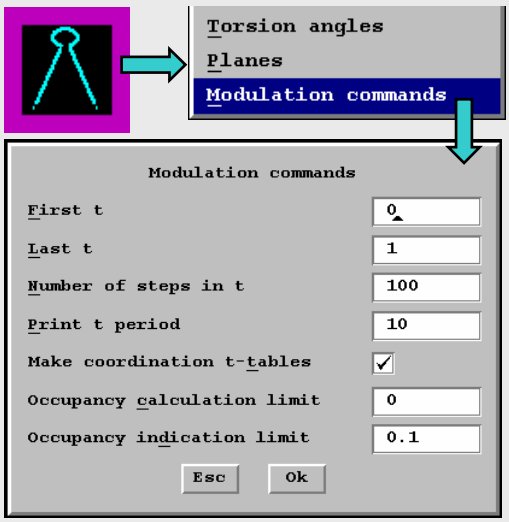


Bond valence coefficients can be checked or redefined





Graphs of x[Na2], y[Na2] and z[Na2] combined into one plot



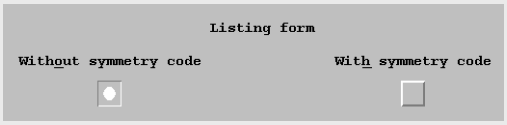
Dist for modulated structures

Distances will be calculated for *t* between 0 and 1 with step 0.01. Every 10th value will be printed to the listing. At the end of the listing coordination tables will be printed for "Central atoms". Occupancy limits are not important for this structure.

The distances "ave", "min" and "max" are evaluated not only from the printed values but from all calculated values of *t*.
The distances after the leading dots correspond to the basic structure, i.e. they do not occur in the real structure.

Distances Na2-O in the listing of Dist

```
**************************
* atom Na1               *
**************************
O1a.........2.4252(9)
 ave         2.4352(13)
 min         2.4138(13)
 max         2.4494(13)
   0.000     2.4450(14)
   0.100     2.4374(13)
   0.200     2.4411(13)
   0.300     2.4144(13)
   0.400     2.4378(14)
   0.500     2.4450(14)
   0.600     2.4374(13)
   0.700     2.4411(13)
   0.800     2.4144(13)
   0.900     2.4378(14)
   1.000     2.4450(14)
--------------------------
O1a.........2.4252(9)
 ave         2.4352(13)
 min         2.4138(13)
 max         2.4494(13)
   0.000     2.4438(14)
   0.100     2.4358(13)
   0.200     2.4484(13)
   0.300     2.4294(13)
   0.400     2.4182(14)
   0.500     2.4438(14)
   0.600     2.4358(13)
   0.700     2.4484(13)
   0.800     2.4294(13)
   0.900     2.4182(14)
   1.000     2.4438(14)
--------------------------
O2a.........2.3123(8)
 ave         2.3263(17)
 min         2.2905(18)
 max         2.3498(17)
   0.000     2.3475(17)
   0.100     2.3434(17)
   0.200     2.3319(17)
   0.300     2.3393(17)
   0.400     2.3165(18)
   0.500     2.2905(18)
   0.600     2.3144(17)
   0.700     2.3356(16)
   0.800     2.3205(16)
   0.900     2.3213(17)
   1.000     2.3475(17)
--------------------------
O2a.........2.3123(8)
 ave         2.3262(17)
 min         2.2906(18)
 max         2.3498(17)
   0.000     2.3349(17)
   0.100     2.3062(17)
   0.200     2.2924(18)
   0.300     2.3247(17)
   0.400     2.3384(18)
   0.500     2.3326(18)
   0.600     2.3466(17)
   0.700     2.3433(16)
   0.800     2.3172(16)
   0.900     2.3248(17)
   1.000     2.3349(17)
--------------------------
O2a.........2.3123(8)
 ave         2.3262(17)
 min         2.2906(18)
 max         2.3498(17)
   0.000     2.3326(18)
   0.100     2.3466(17)
   0.200     2.3433(16)
   0.300     2.3172(16)
   0.400     2.3248(17)
   0.500     2.3349(17)
   0.600     2.3062(17)
   0.700     2.2924(18)
   0.800     2.3247(17)
   0.900     2.3384(18)
   1.000     2.3326(18)
--------------------------
O2a.........2.3123(8)
 ave         2.3257(17)
 min         2.2905(18)
 max         2.3498(17)
   0.000     2.2905(18)
   0.100     2.3144(17)
   0.200     2.3356(16)
   0.300     2.3205(16)
   0.400     2.3213(17)
   0.500     2.3475(17)
   0.600     2.3434(17)
   0.700     2.3319(17)
   0.800     2.3393(17)
   0.900     2.3165(18)
   1.000     2.2905(18)
--------------------------
*
**************************
* atom Na2               *
**************************
O1a.........2.3371(10)
 ave         2.3402(15)
 min         2.3172(14)
 max         2.3556(15)
   0.000     2.3186(14)
   0.100     2.3429(16)
   0.200     2.3519(16)
   0.300     2.3553(16)
   0.400     2.3336(16)
```



This is the used listing form. (*Dist → Basic commands*)

Coordination tables of Na2 in the listing of Dist

```
                                      ************************************
                                      ** Coordination for atom : Na2    **
                                      ************************************

|        t= 0.000        |        t= 0.100        |        t= 0.200        |        t= 0.300
| O2--------- 2.3346(17) | O1--------- 2.3271(14) | O1--------- 2.3175(12) | O2--------- 2.3389(16)
| O2--------- 2.3441(17) | O1--------- 2.3303(14) | O1--------- 2.3189(13) | O1--------- 2.3392(13)
| O1--------- 2.3532(14) | O2--------- 2.3427(17) | O2--------- 2.3430(16) | O1--------- 2.3419(13)
| O1--------- 2.3541(14) | O2--------- 2.3437(17) | O2--------- 2.3431(16) | O2--------- 2.3436(17)
| O2--------- 2.3958(17) | O2--------- 2.4306(17) | O2--------- 2.4293(16) | O2--------- 2.4226(17)
| O2--------- 2.4044(17) | O2--------- 2.4333(17) | O2--------- 2.4295(16) | O2--------- 2.4298(17)

|        t= 0.500        |        t= 0.600        |        t= 0.700        |        t= 0.800
| O2--------- 2.3346(17) | O1--------- 2.3271(14) | O1--------- 2.3175(12) | O2--------- 2.3389(16)
| O2--------- 2.3441(17) | O1--------- 2.3303(14) | O1--------- 2.3189(13) | O1--------- 2.3392(13)
| O1--------- 2.3532(14) | O2--------- 2.3427(17) | O2--------- 2.3430(16) | O1--------- 2.3419(13)
| O1--------- 2.3541(14) | O2--------- 2.3437(17) | O2--------- 2.3431(16) | O2--------- 2.3436(17)
| O2--------- 2.3958(17) | O2--------- 2.4306(17) | O2--------- 2.4293(16) | O2--------- 2.4226(17)
| O2--------- 2.4044(17) | O2--------- 2.4333(17) | O2--------- 2.4295(16) | O2--------- 2.4298(17)

|        t= 1.000        |                        |                        |
| O2--------- 2.3346(17) |                        |                        |
| O2--------- 2.3441(17) |                        |                        |
| O1--------- 2.3532(14) |                        |                        |
| O1--------- 2.3541(14) |                        |                        |
| O2--------- 2.3958(17) |                        |                        |
| O2--------- 2.4044(17) |                        |                        |
```

1.4.3.7 Rigid body refinement

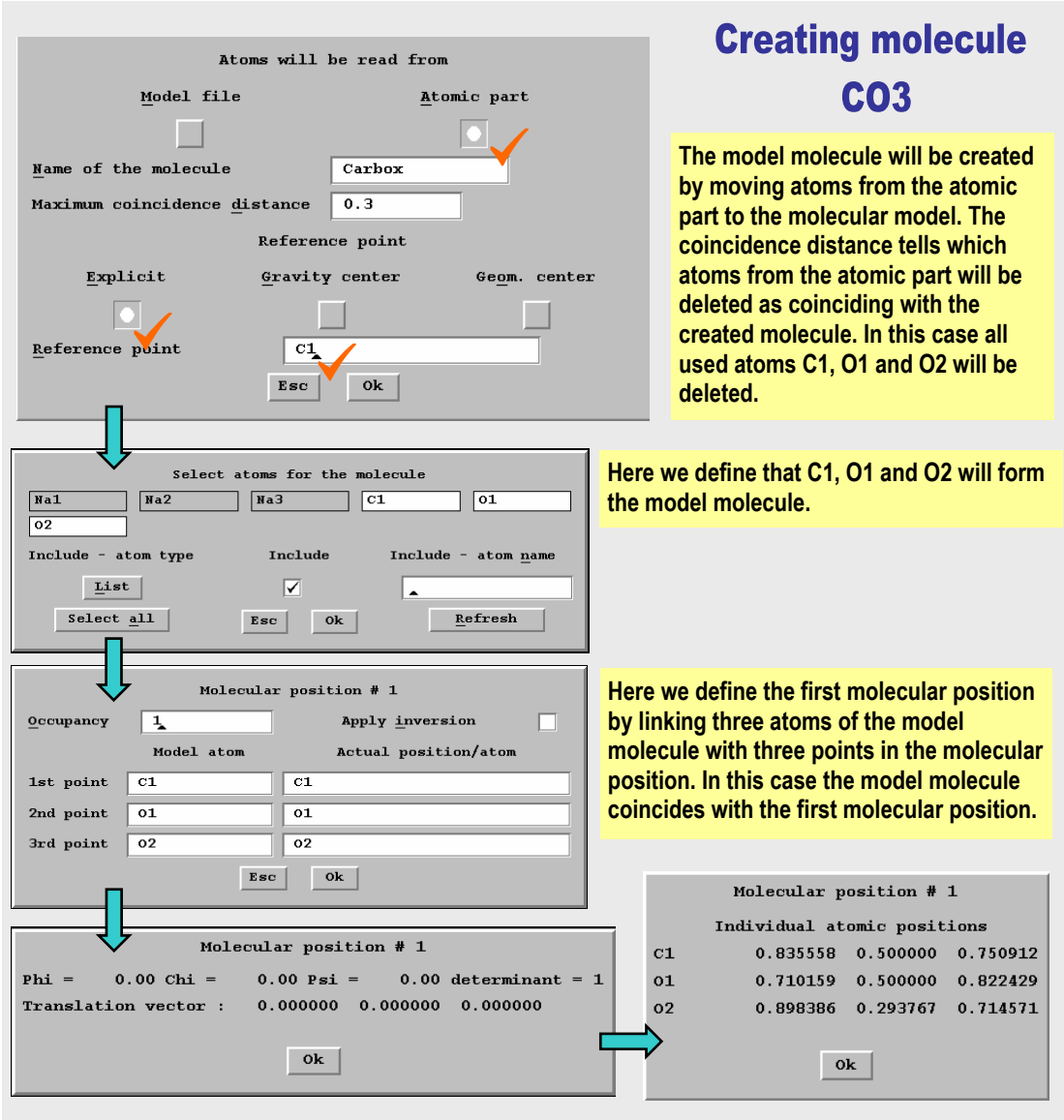
The ideal shape of the chemical group CO_3 is a regular triangle with carbon in its center and with C-O distances all the same. Although we have not used any geometry constraints in our refinement, we can confirm with *Dist* that our result is close to the ideal one. The fact that the covalent bonds within the CO_3 group are much stronger than the bonds to Na atoms should restrict CO_3 modulation to have a molecular character. This means that the modulation does not affect the geometry of the CO_3 that it has a rotation/translation character. This approach will reduce the number of modulation parameters.

Jana2000 describes molecules[1] in the following way. A molecule is defined as a *model molecule* that has one or more *molecular positions*. The positions are determined by translations and rotations that transform the model molecule to the position. The shape of the model molecule can be refined by means of refinement of the atomic parameters of the molecular model. The parameters common for the whole molecule are refined in the rigid group approximation.

Creation of a new molecular part

With *Creation of new molecular part* we can create the model molecule from atoms C1, O1 and O2 that are already available in M40, with the reference point equal to the position of C1. We can use this way of creating molecule only if the atoms in M40 already form the desired fragment – this is why we were rearranging atoms in M40, see § 1.4.2.2 . We create only one position of the molecule at the same place like of the original free atoms of CO_3.

[1] A molecule is understood as a group of atoms for which we want to refine some parameters in the rigid group approximation. It is not necessarily a molecule in the chemical meaning.



After creating the CO_3 molecule the header of M40 changes as shown in the next scheme. The molecular part of M40 starts with name *Carbox* of the model molecule followed by name of the reference point and by atoms of the model. Then the first position *pos#1* follows. It has zero rotations and translations because the atoms of the model molecule are already in the position.

M40 with molecute

First line: the structure consists of 3 free atoms and 1 molecule
Second line: the first molecule has three atoms in one position

```
    3    1    0    1
    3    1
 14.06086 0.000000 0.000000 0.000000 0.000000 0.000000      000000
 0.000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000      000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000      000000
Na1       1  2     0.250000 0.000000 0.000000 0.500000      000  0  4  2
 0.019207 0.015504 0.016901 0.000000 0.007224 0.000000      0000111010

. . . . truncated . . . .

Na3       1  2     0.500000 0.670599 0.000000 0.748044      000  0  4  2
 0.021544 0.025671 0.030642 0.000000 0.008801 0.000000      0101111010
 0.000000 0.065791 0.000000 0.000000-0.005233 0.000000      010010
-0.001030 0.000000-0.001216 0.001529 0.000000 0.004633      101101
 0.000000 0.001257 0.000000 0.000000-0.003953 0.000000      010010
 0.002057 0.000000 0.001327 0.001148 0.000000 0.000281      101101
 0.000000 0.000000 0.000000 0.000313 0.000000-0.001661      000101
 0.000000 0.000000 0.000000 0.004508 0.000000 0.001648      000101
 0.000246 0.000979-0.000616 0.000000-0.000444 0.000000      111010
 0.000396 0.003061 0.000341 0.000000 0.000421 0.000000      111010
 0.000000                                                   0
Carbox    0 1               C1
C1        2  2     0.500000 0.835558 0.500000 0.750912      000  0  4  0
 0.011230 0.012097 0.012383 0.000000 0.004106 0.000000      0000000000
 0.000000 0.056897 0.000000 0.000000 0.000833 0.000000      000000
 0.000745 0.000000-0.001822-0.000796 0.000000 0.000900      000000
 0.000000 0.001094 0.000000 0.000000-0.005470 0.000000      000000
-0.000241 0.000000-0.000053-0.000306 0.000000 0.000506      000000
 0.000000                                                   0
O1        3  2     0.500000 0.710159 0.500000 0.822429      000  0  4  3
 0.014813 0.032277 0.023649 0.000000 0.010302 0.000000      0000000000
 0.000000 0.022970 0.000000 0.000000 0.007949 0.000000      000000
 0.000633 0.000000-0.002709-0.001802 0.000000-0.000063      000000
 0.000000 0.002084 0.000000 0.000000 0.002636 0.000000      000000
-0.000768 0.000000-0.000501 0.000239 0.000000 0.001542      000000
 0.000000 0.000000 0.000000-0.005679 0.000000-0.003558      000000
 0.000000 0.000000 0.000000-0.001710 0.000000 0.000022      000000
 0.001109 0.003446 0.001558 0.000000 0.000771 0.000000      000000
-0.001292 0.000588-0.000820 0.000000-0.001064 0.000000      000000
 0.000000 0.000000 0.000000-0.000541 0.000000-0.000041      000000
 0.000000 0.000000 0.000000 0.001768 0.000000 0.001198      000000
 0.000000                                                   0
O2        3  2     1.000000 0.898386 0.293767 0.714571      000  0  4  3
 0.031890 0.018698 0.029687 0.009588 0.011722-0.000589      0000000000
 0.025769 0.073687 0.020813-0.016333-0.002977-0.034869      000000
 0.001095-0.001947-0.001290-0.000210 0.000089 0.002062      000000
-0.001692 0.000407-0.002597-0.005333-0.009358-0.002429      000000
 0.000299-0.000469 0.000124-0.000561 0.000786-0.000023      000000
-0.003463 0.002704 0.001933 0.003093-0.001293 0.001334      000000
 0.006960-0.001745-0.001478-0.000508 0.000631-0.002452      000000
 0.004113 0.002052 0.004527 0.002762 0.003473 0.001882      000000
 0.002008 0.002769-0.002240 0.002543 0.000234 0.001612      000000
 0.001408-0.000073-0.000260-0.000164-0.000313-0.001336      000000
 0.001649-0.001697-0.000281-0.000767 0.000311-0.000195      000000
 0.000000                                                   0
pos#1     1        1.000000                                000  0  0  0
    0.000    0.000    0.000 0.000000 0.000000 0.000000      0000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
```

Atomic part of M40. Atoms C1, O1 and O2 are no more in this part.

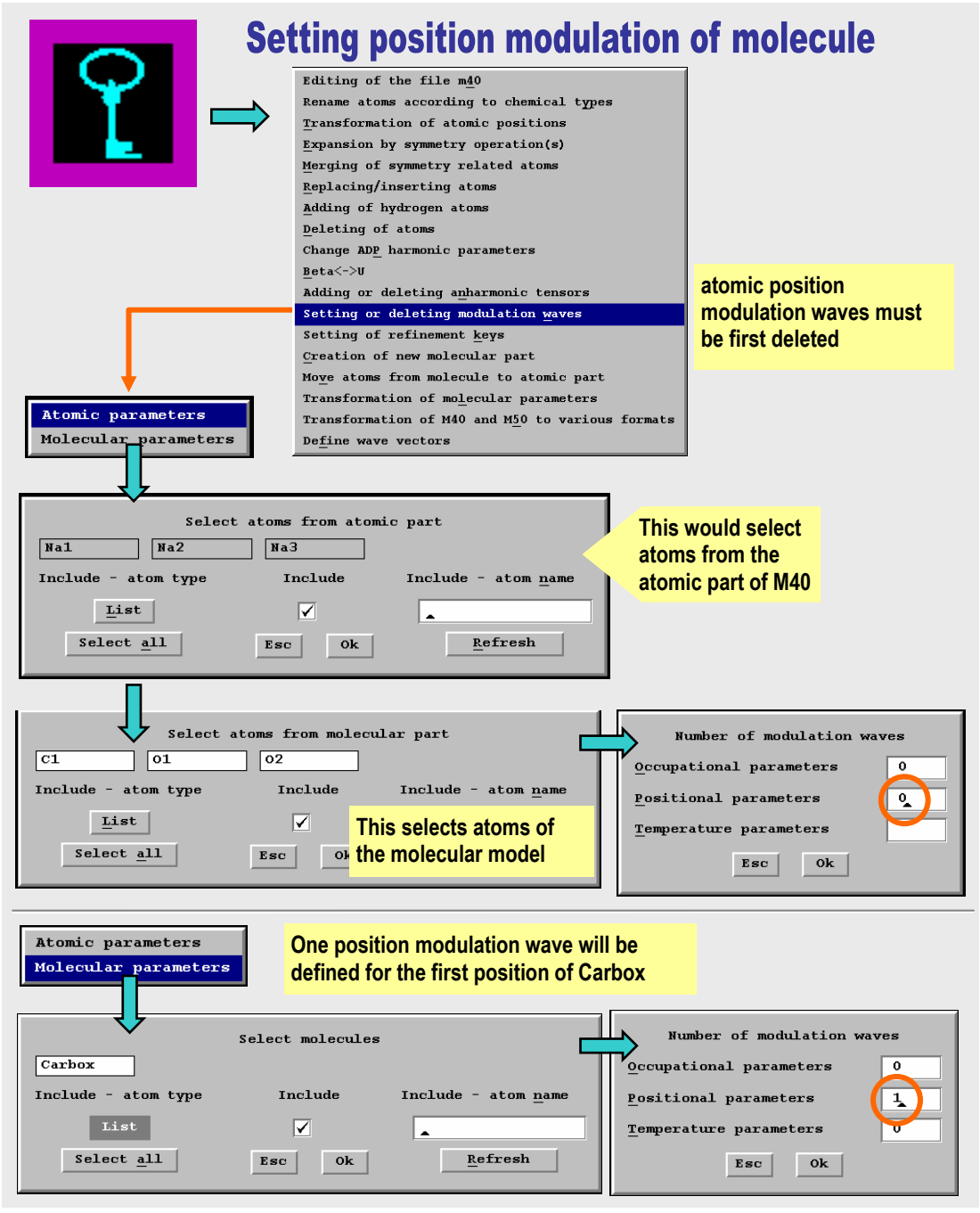
Molecular part of M40. It contains the model molecule "Carbox" with reference point C1. The model molecule consists of atoms C1, O1 and O2. Their atomic parameters can be refined.

The first position of Carbox named "pos#1". The parameters highlighted in bold are three rotations and three translations that transform Carbox to the position. No another molecular parameters are currently refined for this position.

Position modulation of molecule

Jana2000 provides wide flexibility in decision which parameters of the model molecule will be refined in the rigid body approximation. After creation of the molecule by the method described above all parameters are refined as individual atomic parameters of the model molecule except rotations and translations. Because only one molecular position exists, the molecular and atomic descriptions are equivalent. The equivalency can be confirmed by running the zero cycle of *Refine* that yields the same R factors after creation of the molecule.

In the next step, we shall refine position modulation in the rigid body approximation. *Jana2000* does not have a tool for transformation of atomic modulation parameters into molecular ones, as the molecular description cannot fully involve the atomic model[1]. Therefore, we have to first delete all atomic position modulation parameters and then create the first molecular modulation wave.



[1] Transformation of molecular parameters to atomic ones is straightforward and it is included in *Jana2000*.

In M40, we shall see the atoms of the model molecule have no more position modulation parameters. Instead, the position *pos#1* has one position modulation wave. Unlike for free atoms the wave needs 12 parameters, 6 for the rotation part and 6 for the translations. After setting and refining[1] – one by one – four position modulation waves for the molecular position "Pos#1" we get comparable results like those that we have had for the atomic model, but with 24 parameters less.

M40 with a position modulation wave for pos#1

```
Carbox    0 1              C1
C1        2  2     0.500000 0.835558 0.500000 0.750912      000  0  0  0
 0.011230 0.012097 0.012383 0.000000 0.004106 0.000000      0000111010
O1        3  2     0.500000 0.710159 0.500000 0.822429      000  0  0  3
 0.014813 0.032277 0.023649 0.000000 0.010302 0.000000      0101111010
 0.000000 0.000000 0.000000-0.005678 0.000000-0.003558      000101
 0.000000 0.000000 0.000000-0.001710 0.000000 0.000022      000101
 0.001110 0.003447 0.001558 0.000000 0.000771 0.000000      111010
-0.001292 0.000588-0.000820 0.000000-0.001064 0.000000      111010
 0.000000 0.000000 0.000000-0.000541 0.000000-0.000040      000101
 0.000000 0.000000 0.000000 0.001768 0.000000 0.001198      000101
 0.000000                                                   0
O2        3  2     1.000000 0.898386 0.293767 0.714571      000  0  0  3
 0.031890 0.018698 0.029687 0.009588 0.011722-0.000589      0111111111
-0.003464 0.002704 0.001933 0.003093-0.001293 0.001334      111111
 0.006960-0.001744-0.001478-0.000508 0.000631-0.002452      111111
 0.004113 0.002052 0.004527 0.002762 0.003472 0.001883      111111
 0.002008 0.002769-0.002240 0.002543 0.000235 0.001612      111111
 0.001409-0.000073-0.000261-0.000164-0.000314-0.001336      111111
 0.001649-0.001696-0.000281-0.000767 0.000310-0.000196      111111
 0.000000                                                   0
pos#1     1        1.000000                                000  0  1  0
    0.000    0.000    0.000 0.000000 0.000000 0.000000      0000101
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
 0.000100 0.000100 0.000100 0.000100 0.000100 0.000100      111111
 0.000100 0.000100 0.000100 0.000100 0.000100 0.000100      111111
 0.000000                                                   0
```

The atoms of the model molecule have no position modulation.

The molecular position pos#1 has one position modulation wave.

Translation components

Rotation components

[1] This is possible because of very good convergence of sodium carbonate. With structures that are more difficult it would be necessary to remove temperature modulation first, refine the position modulation in the rigid body approximation and then refine the temperature modulation again.

```
Overall R factors : [9850=4016+5834/184]
S(obs) =  1.99 S(all)  =  1.58
R(obs) =  4.31 Rw(obs) =  6.95 R(all) = 12.54 Rw(all) =  8.69
R factors for main reflections : [1155=814+341]
R(obs) =  3.60 Rw(obs) =  7.60 R(all) =  5.02 Rw(all) =  7.97
R factors for satellites of order 1 : [2070=1244+826]
R(obs) =  3.57 Rw(obs) =  4.84 R(all) =  7.19 Rw(all) =  5.72
R factors for satellites of order 2 : [2298=1033+1265]
R(obs) =  5.29 Rw(obs) =  6.67 R(all) = 15.21 Rw(all) =  8.15
R factors for satellites of order 3 : [2044=595+1449]
R(obs) =  7.98 Rw(obs) = 10.46 R(all) = 29.23 Rw(all) = 13.77
R factors for satellites of order 4 : [2283=330+1953]
R(obs) = 11.37 Rw(obs) = 12.28 R(all) = 48.26 Rw(all) = 22.02
Maximum change/s.u. :    0.0430 for U23cos1[O1]
```

Refinement results for the atomic model

```
Overall R factors : [9850=4016+5834/184]
S(obs) =  1.99 S(all)  =  1.58
R(obs) =  4.31 Rw(obs) =  6.95 R(all) = 12.54 Rw(all) =  8.69
R factors for main reflections : [1155=814+341]
R(obs) =  3.60 Rw(obs) =  7.60 R(all) =  5.02 Rw(all) =  7.97
R factors for satellites of order 1 : [2070=1244+826]
R(obs) =  3.57 Rw(obs) =  4.84 R(all) =  7.19 Rw(all) =  5.72
R factors for satellites of order 2 : [2298=1033+1265]
R(obs) =  5.29 Rw(obs) =  6.67 R(all) = 15.21 Rw(all) =  8.15
R factors for satellites of order 3 : [2044=595+1449]
R(obs) =  7.98 Rw(obs) = 10.46 R(all) = 29.23 Rw(all) = 13.77
R factors for satellites of order 4 : [2283=330+1953]
R(obs) = 11.37 Rw(obs) = 12.28 R(all) = 48.26 Rw(all) = 22.02
Maximum change/s.u. :    0.0452 for U23cos1[O1]
```

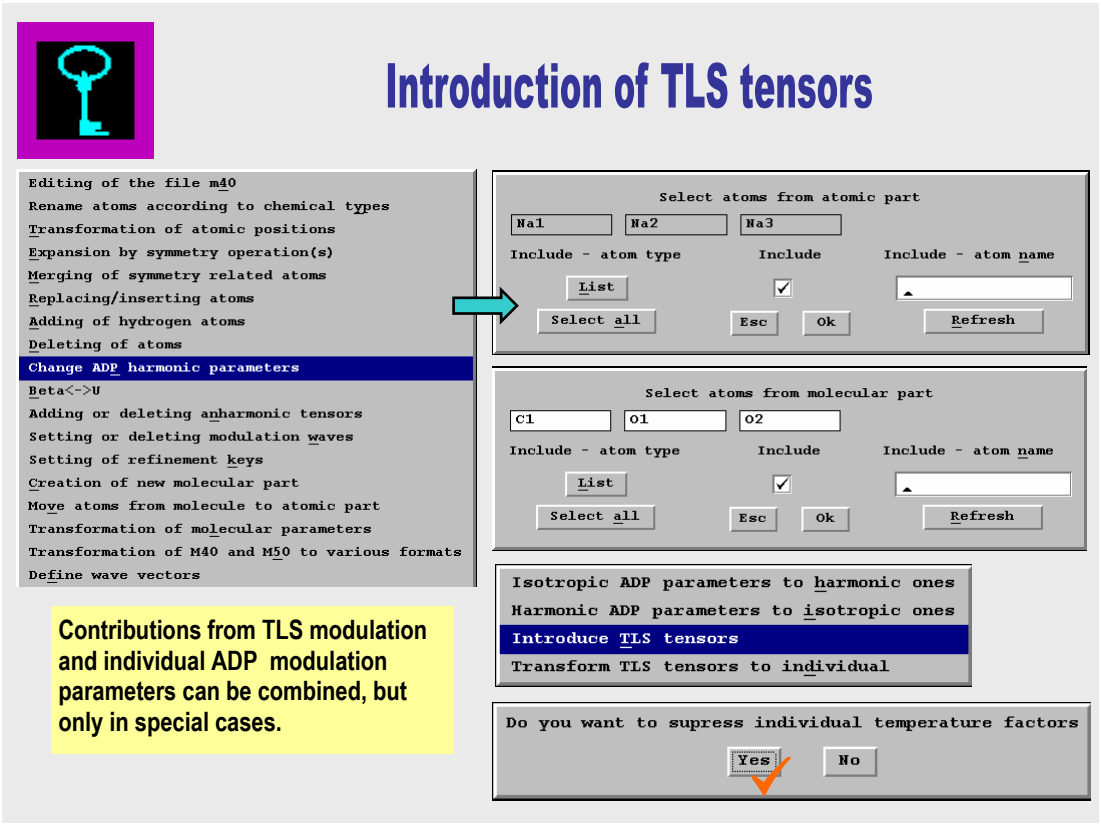
Refinement results with the initial molecule (should be the same)

```
Overall R factors : [9850=4016+5834/160]
S(obs) =  2.16 S(all)  =  1.67
R(obs) =  4.60 Rw(obs) =  7.54 R(all) = 12.83 Rw(all) =  9.20
R factors for main reflections : [1155=814+341]
R(obs) =  3.66 Rw(obs) =  7.67 R(all) =  5.09 Rw(all) =  8.04
R factors for satellites of order 1 : [2070=1244+826]
R(obs) =  3.84 Rw(obs) =  5.28 R(all) =  7.46 Rw(all) =  6.11
R factors for satellites of order 2 : [2298=1033+1265]
R(obs) =  5.81 Rw(obs) =  7.67 R(all) = 15.72 Rw(all) =  9.00
R factors for satellites of order 3 : [2044=595+1449]
R(obs) =  8.67 Rw(obs) = 11.24 R(all) = 29.80 Rw(all) = 14.45
R factors for satellites of order 4 : [2283=330+1953]
R(obs) = 12.80 Rw(obs) = 14.82 R(all) = 48.89 Rw(all) = 23.44
Maximum change/s.u. :   -0.0084 for U12cos1[Na3]
```

Refinement results with molecular position modulation

Displacement parameters of molecule

Until now, we refined individual ADP for all atoms of the model molecule. In a rigid group description, we can use TLS tensors and their modulations instead, assuming that all atoms of the molecule move in phase. In the first step, we shall introduce the TLS tensors instead of individual ADP ellipsoids, but the ADP modulation will be still calculated for individual atoms.



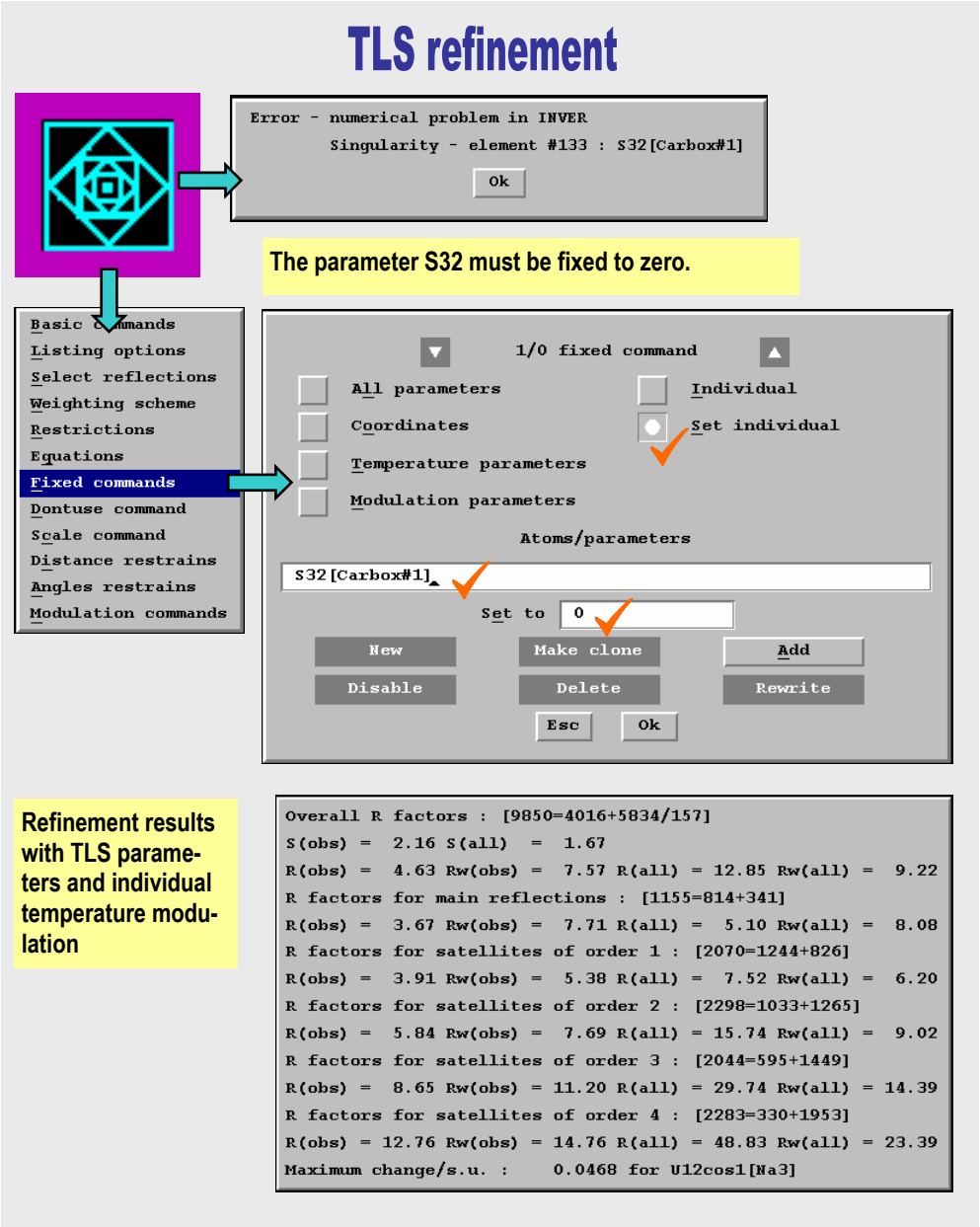
In M40, there are now no individual ADP in the model molecule. Amidst the molecular parameters of *pos#1* there are new 21 parameters, six for the tensor *T*, six for *L* and nine for *S*. In fact, there is no saving of parameters by introducing TLS, as our CO_3 group is too small.

```
Carbox    0 1              C1
C1        2  0     0.500000 0.835558 0.500000 0.750912      000  0  0  0
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000      0000111010
O1        3  0     0.500000 0.710195 0.500000 0.822463      000  0  0  3
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000      0101111010
 0.000000 0.000000 0.000000-0.005675 0.000000-0.003515      000101
 0.000000 0.000000 0.000000-0.001667 0.000000-0.000083      000101
 0.001083 0.003881 0.001791 0.000000 0.001024 0.000000      111010
-0.001759 0.000766-0.001053 0.000000-0.001242 0.000000      111010
 0.000000 0.000000 0.000000-0.000650 0.000000 0.000073      000101
 0.000000 0.000000 0.000000 0.001927 0.000000 0.001332      000101
 0.000000                                                   0
O2        3  0     1.000000 0.898428 0.293902 0.714727      000  0  0  3
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000      0111111111
-0.003203 0.002717 0.002113 0.003034-0.001085 0.001302      111111
 0.007449-0.002021-0.001254-0.000568 0.000871-0.002642      111111
 0.004236 0.001891 0.004518 0.002861 0.003331 0.001822      111111
 0.002121 0.002837-0.002442 0.002410 0.000171 0.001577      111111
 0.001583-0.000843-0.000067-0.000325-0.000190-0.001243      111111
 0.001826-0.002186-0.000737-0.000726 0.000507-0.000792      111111
 0.000000                                                   0
pos#1     1        1.000000                                 000  0  4  0
    0.000    0.000    0.000-0.000016 0.000000-0.000046      0000101
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
 0.002892 0.008655 0.006930 0.000000 0.000000 0.000000      111111
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000      111111
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000      111111
 0.000000 0.000000 0.000000                                 110
 0.000000 0.056798 0.000000 0.000000 0.000676 0.000000      010010
 0.001059 0.000000-0.001639-0.000823 0.000000 0.001244      101101
 0.000000 0.000954 0.000000 0.000000-0.005366 0.000000      010010
-0.000062 0.000000 0.000100-0.000420 0.000000 0.000425      101101
-0.008560 0.000000 0.031808 0.019237 0.000000-0.016429      101101
 0.000000-0.000962 0.000000 0.000000-0.001310 0.000000      010010
 0.001415 0.000000-0.001770 0.000636 0.000000-0.006803      101101
 0.000000-0.001056 0.000000 0.000000 0.001231 0.000000      010010
 0.000000                                                   0
```

The atoms of the model molecule have no individual ADP except their modulation.

Parameters of the newly introduced tensors T (1st line), L (2nd line) and S (remaining nine parameters).

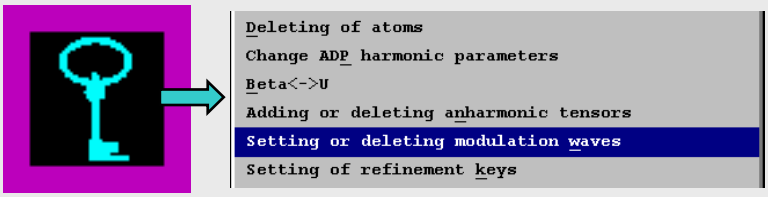
When we start refinement of the structure model with TLS parameters *Refine* exits soon with an error message concerning the parameter *S32*. [1] To continue we must fix the parameter to zero using *Fixed command*. The R-values after the refinement are very similar to the model without TLS. Note that the ADP modulation parameters are still calculated independently for individual atoms.



Finally, we shall accomplish the rigid body refinement by refinement of TLS modulation. Like in the case of molecular position modulation, the ADP modulation waves must be first deleted in the atomic part and then initialized in the molecular part. During the refinement, it will be necessary to fix parameters *S13sin1*, *S13cos1*, *S32sin2* and *S32cos2*.[2] The third TLS modulation wave cannot be refined because of strong correlations between L and S components. The R-values slightly increase but they are still comparable with the atomic model.

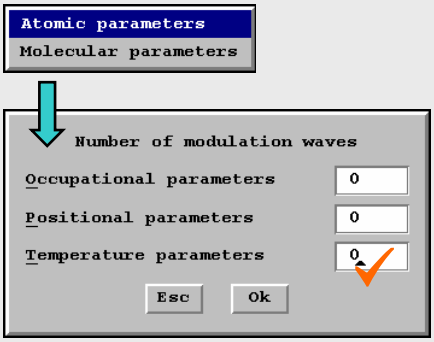
[1] The names of all structure parameters are given in the chapter **Error! Reference source not found.** , page **Error! Bookmark not defined.**.

[2] We can use wildcards and fix parameters S13???1[Carbox#1], S32????2[Carbox#1].

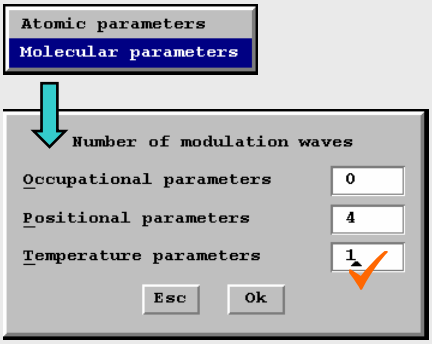


TLS modulation

Deleting of individual temperature modulation waves



Setting of one TLS modulation wave for the first position of Carbox




```
Overall R factors : [9850=4016+5834/141]
S(obs) =  2.37 S(all)  =  1.79
R(obs) =  5.19 Rw(obs) =  8.32 R(all) = 13.40 Rw(all) =  9.88
R factors for main reflections : [1155=814+341]
R(obs) =  3.89 Rw(obs) =  8.00 R(all) =  5.31 Rw(all) =  8.37
R factors for satellites of order 1 : [2070=1244+826]
R(obs) =  4.74 Rw(obs) =  6.94 R(all) =  8.36 Rw(all) =  7.62
R factors for satellites of order 2 : [2298=1033+1265]
R(obs) =  6.74 Rw(obs) =  8.64 R(all) = 16.68 Rw(all) =  9.88
R factors for satellites of order 3 : [2044=595+1449]
R(obs) =  9.23 Rw(obs) = 11.53 R(all) = 30.30 Rw(all) = 14.72
R factors for satellites of order 4 : [2283=330+1953]
R(obs) = 12.38 Rw(obs) = 13.39 R(all) = 48.51 Rw(all) = 22.62
Maximum change/s.u. :    0.0192 for L11sin2[Carbox#1]
```

Refinement results with TLS parameters and their modulation

M40 with TLS modulation

```
Carbox    0 1              C1
C1        2  0     0.500000 0.835558 0.500000 0.750912      000  0  0  0
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000      0000000000
O1        3  0     0.500000 0.710216 0.500000 0.822498      000  0  0  0
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000      0101000000
O2        3  0     1.000000 0.898442 0.293910 0.714712      000  0  0  0
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000      0111000000
pos#1     1        1.000000                                 000  0  4  1
    0.000    0.000    0.000-0.000024 0.000000-0.000053      0000101
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
 0.002914 0.008936 0.006748 0.000000 0.001453 0.000000      111010
 0.003023 0.005662 0.008688 0.000000 0.000008 0.000000      111010
 0.000000 0.000016 0.000000 0.000068 0.000000 0.000000      010100
 0.000000 0.000389 0.000000                                 010
 0.000000 0.056799 0.000000 0.000000 0.000621 0.000000      010010
 0.001049 0.000000-0.001646-0.000829 0.000000 0.001243      101101
 0.000000 0.000936 0.000000 0.000000-0.005430 0.000000      010010
-0.000090 0.000000 0.000087-0.000343 0.000000 0.000334      101101
-0.008558 0.000000 0.031850 0.019250 0.000000-0.016419      101101
 0.000000-0.000959 0.000000 0.000000-0.001313 0.000000      010010
 0.001423 0.000000-0.001738 0.000600 0.000000-0.006843      101101
 0.000000-0.000928 0.000000 0.000000 0.001375 0.000000      010010
 0.000010 0.000010 0.000010 0.000010 0.000010 0.000010      111111
 0.000010 0.000010 0.000010 0.000010 0.000010 0.000010      111111
 0.000010 0.000010 0.000010 0.000010 0.000010 0.000010      111111
 0.000010 0.000010 0.000010 0.000010 0.000010 0.000010      111111
 0.000010 0.000010 0.000010 0.000010 0.000010 0.000010      111111
 0.000010 0.000010-0.000020                                 110
 0.000010 0.000010 0.000010 0.000010 0.000010 0.000010      111111
 0.000010 0.000010-0.000020                                 110
 0.000000
```

TLS parameters

position modulation parameters

TLS modulation parameters

1.5 Modulated structure from powder

In this chapter, we present solution of modulated structure $NbTe_4$ [5] from home lab powder data. The sample was measured for testing purposes to compare results from Rietveld refinement with parameters of the same structure solved from single crystal data in 1986 [8].

Used technique	Bragg-Brentano geometry with Philips X'pert diffractometer. A thin layer of powder dispersed on a flat-plate holder
Absorption correction	none
Profile data format	GSAS
Cell parameters	a=6.499Å, c=6.837Å
Radiation:	monochromatic CuKα1, perpendicular setting
Space group	P4/mcc
q vector	(½,½,0.691)
Superspace group	P4/mcc(½½γ)
Chemical formula	$NbTe_4$, Z=2

The profile data are available in the Jana Web page as **nbte1.zip**.[1]

1.5.1 Profile refinement

In *EditM50* we define the cell parameters, number of dimensions (4) and **q** vector, the superspace symmetry, type of radiation, chemical composition and atomic form factors. Then we import the data in GSAS format. In *Powder options*, subwindow *Sample*, we select as the used technique *Symmetrical reflection* with the implicit value of the limit absorption[2].

In the profile refinement, we first refine 15 *Legendre* polynomials and *Shift*. Then we add refinement of Gaussian parameters *GW*, *GU* and *GV*. R_p drops to 22.5%. *GV* can be fixed to zero without increase of R_p. In the next step, we refine pseudo-Voigt profile *GW*, *GU, LX* and *LY* and R_p lowers to 19.1%. We find that *GU* can also be fixed to zero. Refinement of cell parameters and **q** vector yields $R_p \approx 14\%$. For refinement of **q** vector, we take into the account only the first order satellites by defining *m* in *Powder options* →*Cell* subwindow.

At this stage of refinement, a careful inspection of the powder profile reveals two problems. Firstly, the peaks are affected by asymmetry that is clearly visible for instance for the reflection *1 0 0 0* at 2θ=13.6º. Secondly, if we enlarge[3] the basis of the peak *2 1 1 0* at 2θ=33.5º, we see the used *cutoff* of eight *FWHM*[4] is too small. The value about 16 considerably reduces the problem[5].

For refinement of the profile asymmetry, we shall use the *divergence* method. The parameters *S/L* and *H/L* are strongly correlated and some restriction is almost always necessary. Otherwise, the refinement fails when *S/L* reaches the value of *H/L*. For this case we can use an equation *H/L = S/L*. The final value of R_p will be 13.2%. It is not changed if we use also the second order satellites in the profile refinement even though they are known to exist from the single crystal measurement.

---

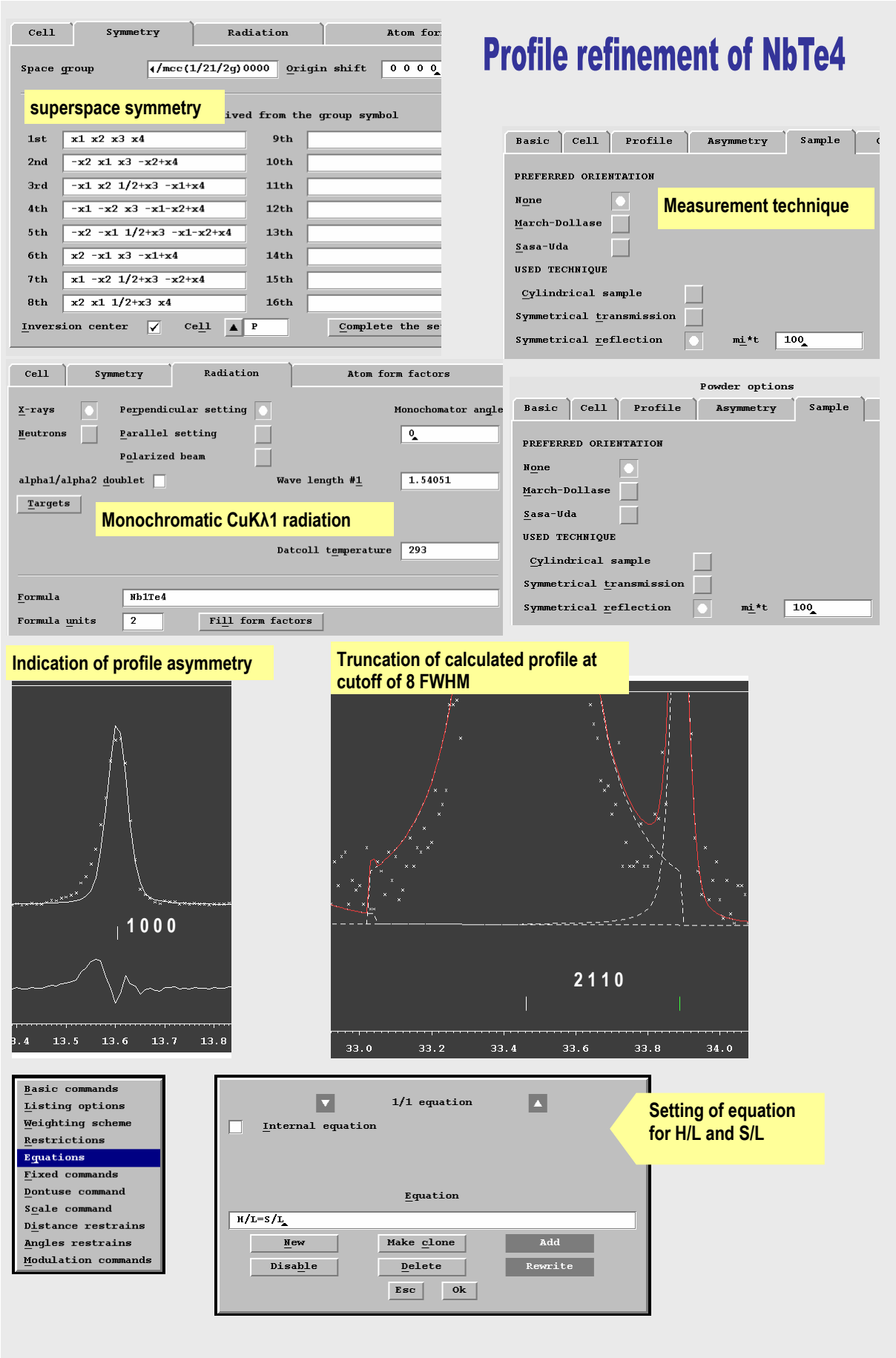
[1] http://www-xray.fzu.cz/jana/Jana2000/manual/examples/nbte1.zip

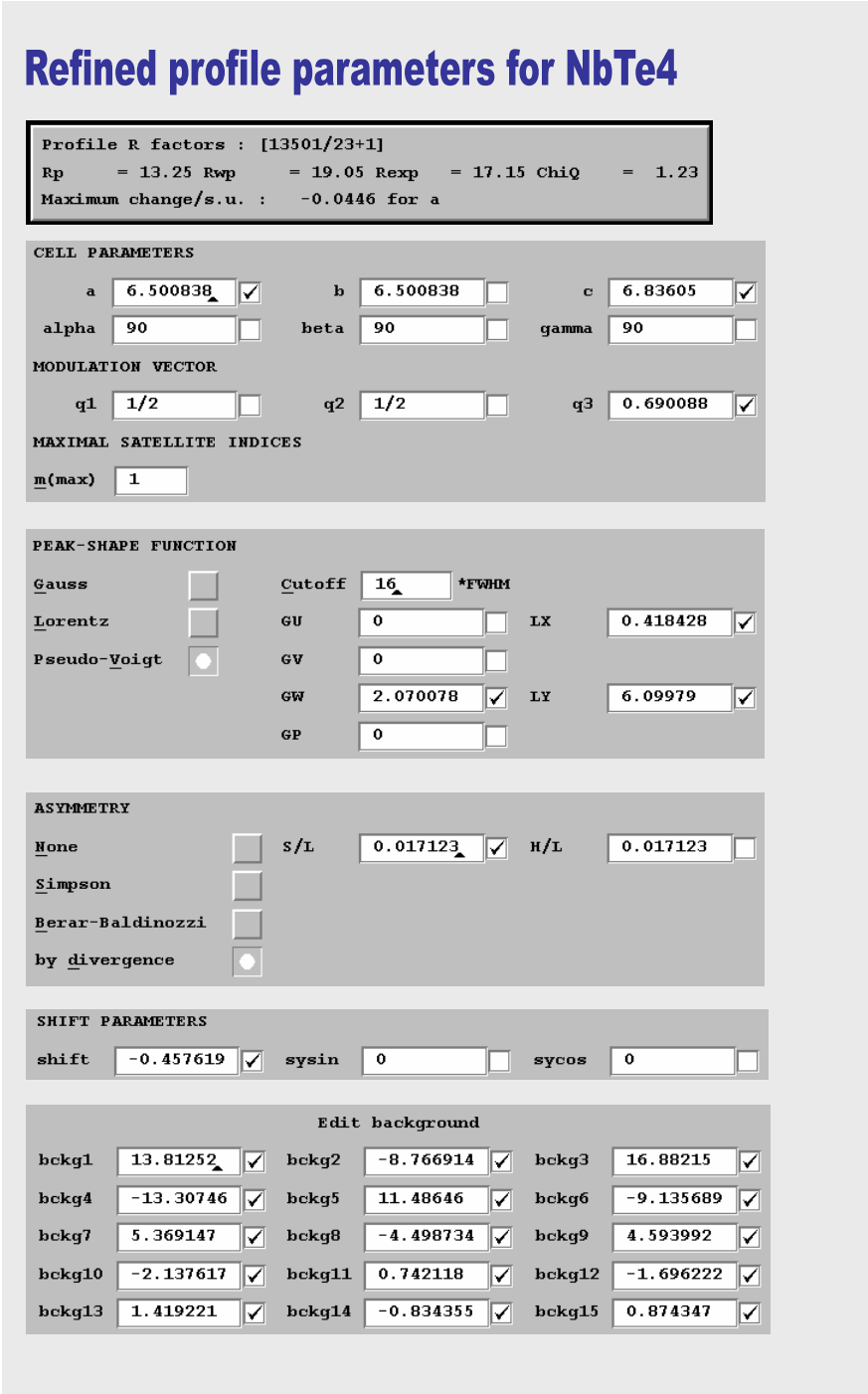
[2] The large μt means that the sample has negligible transparency.

[3] For this the plotting of difference curve must be disabled in *Options* of the *Profile viewer* and plotting of component curves must be activated through the button *Details*.

[4] Full Width at Half Maximum.

[5] However, if we enlarge sufficiently the plot we shall always see the cut.


Profile refinement of NbTe4
Cell
Symmetry
Radiation
Atom for
Space group
/mcc(1/21/2g)0000
Origin shift
0 0 0 0
superspace symmetry
ived from the group symbol
1st x1 x2 x3 x4
2nd -x2 x1 x3 -x2+x4
3rd -x1 x2 1/2+x3 -x1+x4
4th -x1 -x2 x3 -x1-x2+x4
5th -x2 -x1 1/2+x3 -x1-x2+x4
6th x2 -x1 x3 -x1+x4
7th x1 -x2 1/2+x3 -x2+x4
8th x2 x1 1/2+x3 x4
9th
10th
11th
12th
13th
14th
15th
16th
Inversion center
Cell
P
Complete the se
Basic
Cell
Profile
Asymmetry
Sample
PREFERRED ORIENTATION
None
March-Dollase
Sasa-Uda
USED TECHNIQUE
Cylindrical sample
Symmetrical transmission
Symmetrical reflection
mi*t
100
Measurement technique
Cell
Symmetry
Radiation
Atom form factors
X-rays
Neutrons
Perpendicular setting
Parallel setting
Polarized beam
Monochromator angle
0
alpha1/alpha2 doublet
Wave length #1
1.54051
Targets
Monochromatic CuKλ1 radiation
Datcoll temperature
293
Formula
NbiTe4
Formula units
2
Fill form factors
Powder options
Basic
Cell
Profile
Asymmetry
Sample
PREFERRED ORIENTATION
None
March-Dollase
Sasa-Uda
USED TECHNIQUE
Cylindrical sample
Symmetrical transmission
Symmetrical reflection
mi*t
100
Indication of profile asymmetry
1000
13.4
13.5
13.6
13.7
13.8
Truncation of calculated profile at cutoff of 8 FWHM
2110
33.0
33.2
33.4
33.6
33.8
34.0
Basic commands
Listing options
Weighting scheme
Restrictions
Equations
Fixed commands
Dontuse command
Scale command
Distance restrains
Angles restrains
Modulation commands
1/1 equation
Internal equation
Equation
H/L=S/L
New
Make clone
Add
Disable
Delete
Rewrite
Esc
Ok
Setting of equation for H/L and S/L

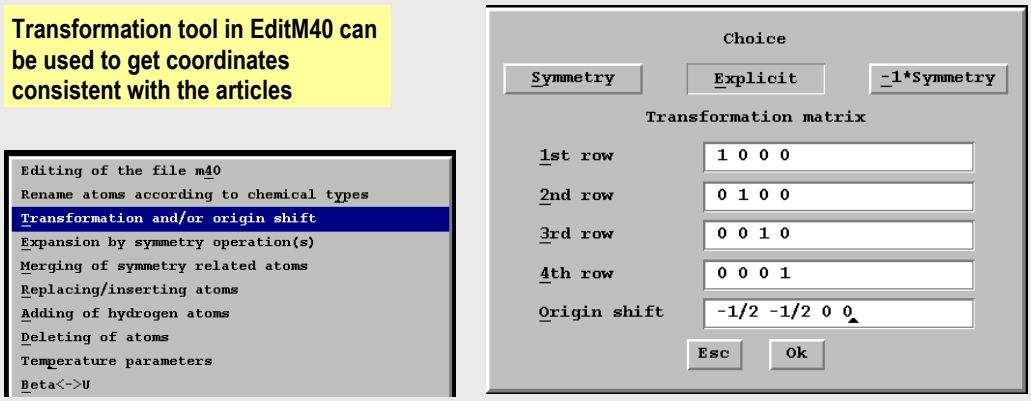


1.5.2 Average structure

With refined profile parameters, we can call the external program *EXPO* [2] for solution of the structure by direct methods. It returns several equivalent solutions that we should transform to the one with Nb at (0,0,¼) and Te at (0.33,-0.17,½) that are consistent with the articles [5] and [8]. The refinement with isotropic ADP converges to R_{obs}≈10.9% and R_p≈18.9%. Using of harmonic ADP would improve the fit significantly, but unfortunately, the refined parameters are not positive definite.

Average structure of NbTe4

Transformation tool in EditM40 can be used to get coordinates consistent with the articles



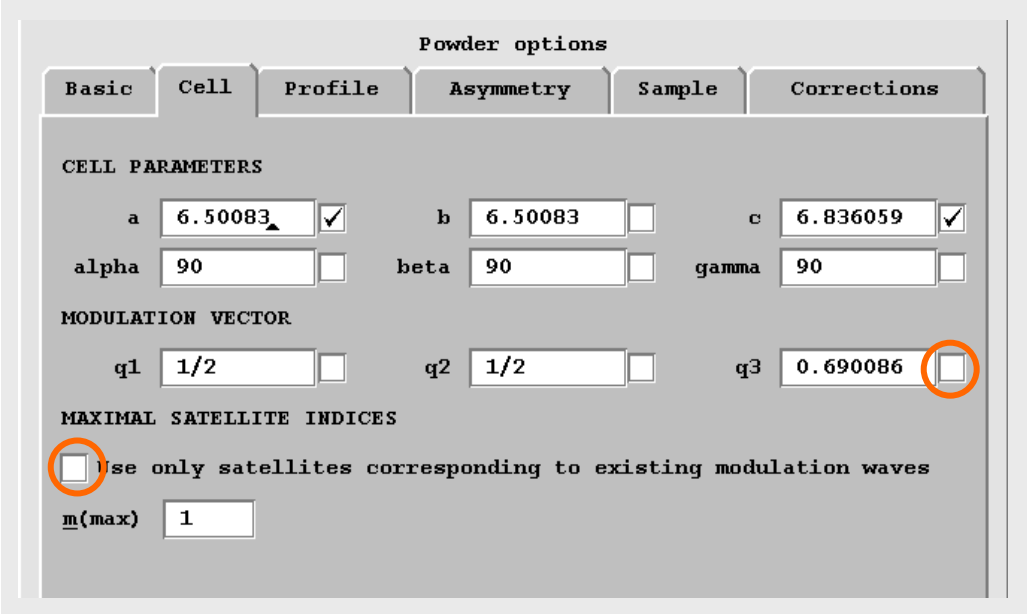

```
Overall R factors : [433=131+302/5]
R(obs) = 10.88 Rw(obs) =  9.73 R(all) = 11.01 Rw(all) =  9.74
R factors for main reflections : [155=131+24]
R(obs) = 10.88 Rw(obs) =  9.73 R(all) = 11.01 Rw(all) =  9.74
Profile R factors : [13501/22+5]
Rp     = 18.87 Rwp     = 25.38 Rexp   = 17.15 ChiQ    =  2.19
Maximum change/s.u. :   -0.0411 for shift
```

Final R values

M40 with the refined average structure

```
   2    0    0    0
 0.057636 0.000000 0.000000 0.000000 0.000000 0.000000      100000
 0.000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000      000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000      000000
Te1       2  1     0.500000 0.328389-0.145752 0.000000      000  0  0  0
 0.000615 0.000000 0.000000 0.000000 0.000000 0.000000      0110100000
Nb1       1  1     0.125000 0.000000 0.000000 0.250000      000  0  0  0
 0.008567 0.000000 0.000000 0.000000 0.000000 0.000000      0000100000
```

For the average structure, we must not refine **q** vector as the contributions to calculated satellite intensities are zero. We can check in the *Powder options* that the program fixes **q** vector automatically. For refinement of modulated structure we can choose *Use only satellites corresponding to existing modulation waves* that has similar meaning.



1.5.3 Modulated structure

For refinement of modulated structure, a transformation is convenient that removes the rational components of the **q** vector[1]. As α and β of **q** vector equals to ½ the cell must be transformed by matrix

$$\begin{pmatrix} 1 & 1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

that applies to the cell vector in the direct space expressed as a row vector. The transformation doubles the cell, introduces the C centering and changes **q** vector to the form (0,1,γ). Another transformation changes **q** vector to the desired form of (0,0,γ). In the same time the centering C(½,½,0,0) becomes X(½,½,0,½)[2]. In *Jana2000*, all these transformations are done automatically as shown in the next scheme.

Refinement of the first position modulation wave converges smoothly and improves essentially both R_p and R_{obs} factors. At the beginning, it needs damping about 0.1 that can be later changed to 0.5. However, the isotropic ADP become negative. Because of wrong ADP, a question arises about reliability of modulation parameters. This can be answered by comparison of the position modulation parameters for various models. They are stable and in agreement with the single crystal parameters. A similar test can be used to show that the second order position modulation wave cannot be reliably refined from our powder data.

Comparison of modulation parameters for various structure models

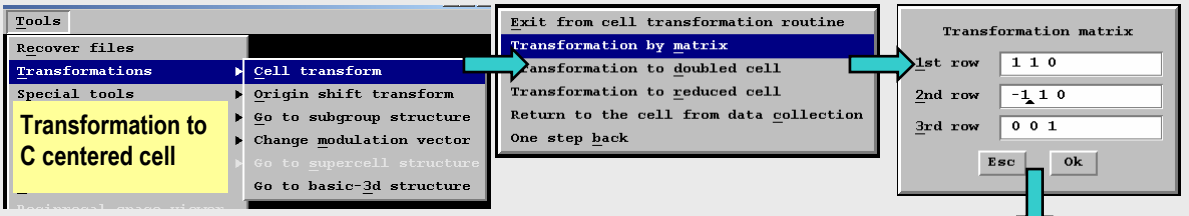
Model[3]	zsin1[Te1]	xcos1[Te1]	ycos1[Te1]	zsin1[Nb1]
1986	0.006	-0.013	0.007	0.039
iso<0	0.008	-0.013	0.007	0.043
iso=0.003	0.007	-0.013	0.006	0.039
aniso1	0.007	-0.014	0.006	0.038
aniso2	0.007	-0.014	0.007	0.039

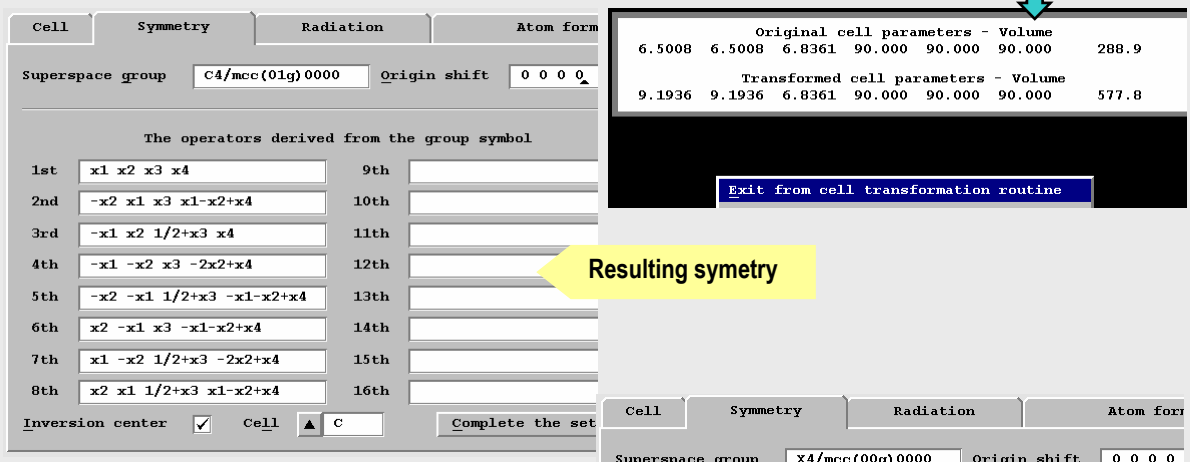
[1] Rational components would introduce non-linear correlations between positions and modulation amplitudes.

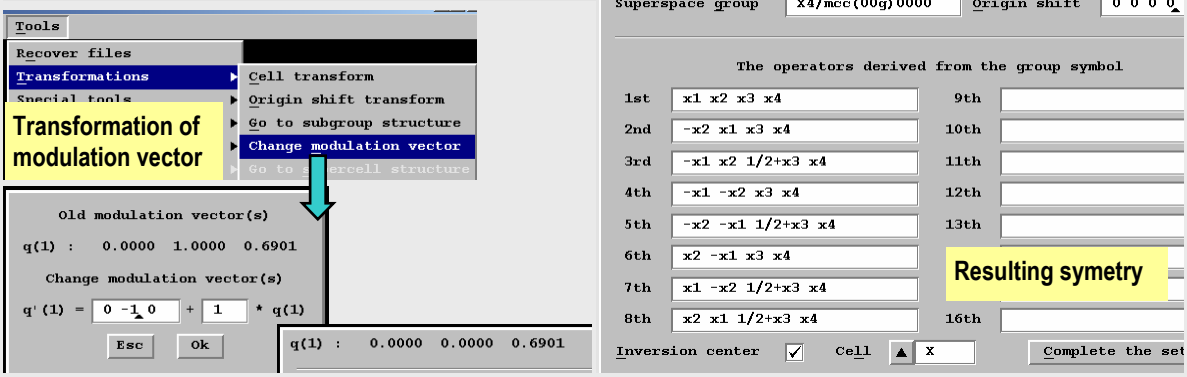
[2] In Jana2000, X denotes non-standard centering.

[3] "1986" … single crystal refinement from [8]; "iso<0" … refinement with isotropic temperature parameters that were negative; "iso=0.003" … refinement with isotropic temperature parameters fixed to 0.003; "aniso1" … refinement with anisotropic temperature parameters and one position modulation wave; "aniso2" … refinement with anisotropic temperature parameters and two position modulation waves.

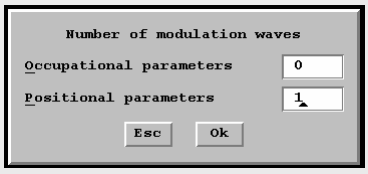
Refinement of modulated structure

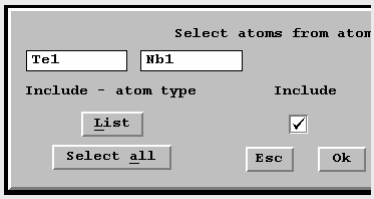






Refinement of one position modulation wave






```
Overall R factors : [433=347+86/9]
R(obs) =  8.62 Rw(obs) =  9.25 R(all) =  8.90 Rw(all) =  9.29
R factors for main reflections : [155=141+14]
R(obs) =  8.15 Rw(obs) =  8.78 R(all) =  8.26 Rw(all) =  8.79
R factors for satellites of order 1 : [278=206+72]
R(obs) =  9.85 Rw(obs) = 10.59 R(all) = 10.33 Rw(all) = 10.70
Profile R factors : [13501/22+9]
Rp     = 17.02 Rwp     = 22.45 Rexp   = 17.15 ChiQ    =  1.71
Maximum change/s.u. :    0.0410 for zsin1[Nb1]
```

R factors with one position modulation wave and isotropic temperature parameters

```
Te1       2  1     0.500000 0.236844 0.091560 0.000000      000  0  1  0
-0.003081 0.000000 0.000000 0.000000 0.000000 0.000000      0110100000
 0.000000 0.000000 0.007631-0.013175 0.006525 0.000000      001110
 0.000000                                                   0
Nb1       1  1     0.125000 0.000000 0.000000 0.250000      000  0  1  0
-0.007508 0.000000 0.000000 0.000000 0.000000 0.000000      0000100000
 0.000000 0.000000 0.042479 0.000000 0.000000 0.000000      001000
 0.000000                                                   0
```

Final structure parameters

```
Overall R factors : [433=345+88/17]
R(obs) =  6.79 Rw(obs) =  7.39 R(all) =  7.19 Rw(all) =  7.43
R factors for main reflections : [155=139+16]
R(obs) =  6.60 Rw(obs) =  7.18 R(all) =  6.75 Rw(all) =  7.20
R factors for satellites of order 1 : [278=206+72]
R(obs) =  7.27 Rw(obs) =  8.03 R(all) =  8.18 Rw(all) =  8.13
Profile R factors : [13501/22+17]
Rp     = 15.73 Rwp     = 21.20 Rexp   = 17.14 ChiQ    =  1.53
Maximum change/s.u. :   -0.0463 for y[Te1]
```

R factors with two position modulation waves and

1.6 Advanced powder refinement

In this chapter, we present solution of a modulated structure PbO [9] from powder data measured with synchrotron radiation at 90K. In the sample, there is an admixture of a non-modulated phase of PbO that can be filtered-out with help of the multiphase refinement.

Used technique	Cylindrical sample (Debye-Scherer)
Absorption coefficient μr	0.2
Profile data format	M92 (JANA)
	Phase I (modulated)
Cell parameters	a=5.610Å, b=5.608Å, c=4.998Å, α=β=γ=90°
Radiation:	Synchrotron λ=0.3507Å
Space group	Cmma
q vector	(0, 0.370, 0)
Superspace group	Cmma(0β0)s
Chemical formula	PbO, Z=4
	Phase II (admixture)
Cell parameters	a=5.482Å, b=4.725Å, c=5.887Å, α=β=γ=90°
Space group	Pbma
Chemical formula	PbO, Z=4
Coordinates	Pb1_b(-0.0208 0.25 0.2309) O1_b(0.0886 0.25 -0.1309)

The profile data are available in the Jana Web page as **pbo1.zip**.[1]

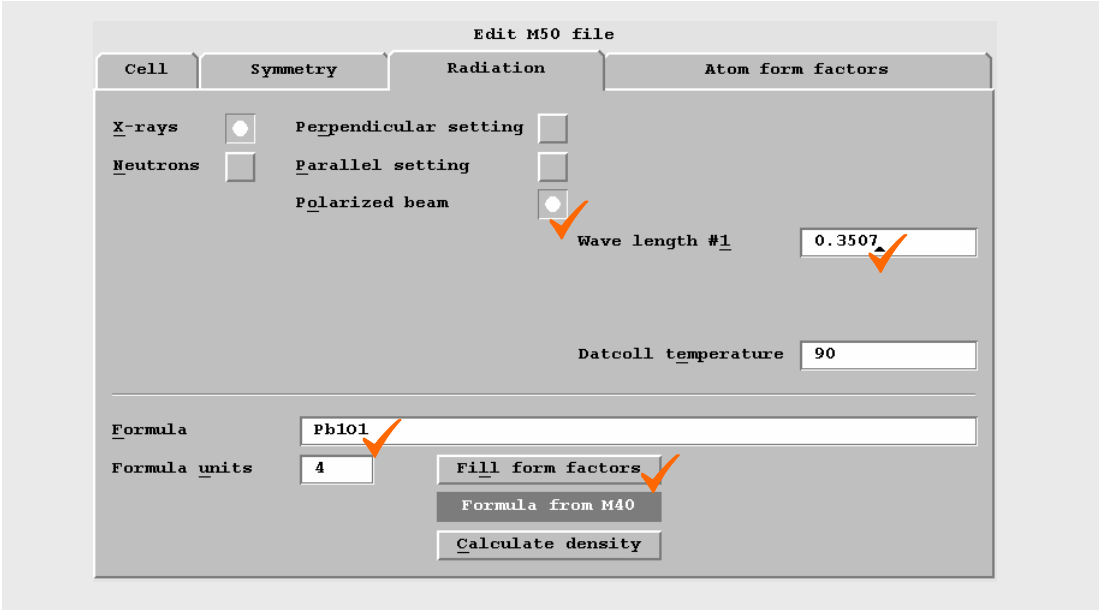
1.6.1 Profile refinement

1.6.1.1 Basic profile

The preliminary work is similar like for the example of simple powder structure, see § 1.3 page 41. In *Jana2000* the anomalous scattering coefficients *f'* and *f''* are automatically available for general wavelength, i.e. also for the synchrotron radiation used for the measurement of our data.

At the beginning, we define a three-dimensional structure with parameters as given in the table. Then we import the powder data pbo1.dat. The following figure shows how the synchrotron radiation is selected in *EditM40*. The information about the temperature of the data collection is used only for the CIF output and for plotting of potential curves by *Contour*.

[1] http://www-xray.fzu.cz/jana/Jana2000/manual/examples/pbo1.zip



The profile refinement is not so straightforward like in the previous powder example. At the beginning, we refine 15 background parameters (*Legendre polynomial*) and *Shift*. Then we refine parameter *GW* and the pseudo-Voigt profile *GU*, *GW*, *LX* and *LY*[1] . For refinement of cell parameters we must first define an equation *b=a* because the crystal has pseudo tetragonal character. Finally, we define μr for the absorption correction that however does not affect profile refinement. All refinements can be done without damping.

When we zoom in the basis of a strong reflection in the *Profile viewer*[2] we see its contributions are truncated. Henceforward in this example we shall use *cutoff* 12 *FWHM*[3]. The R_p value at this point should be about 13%.

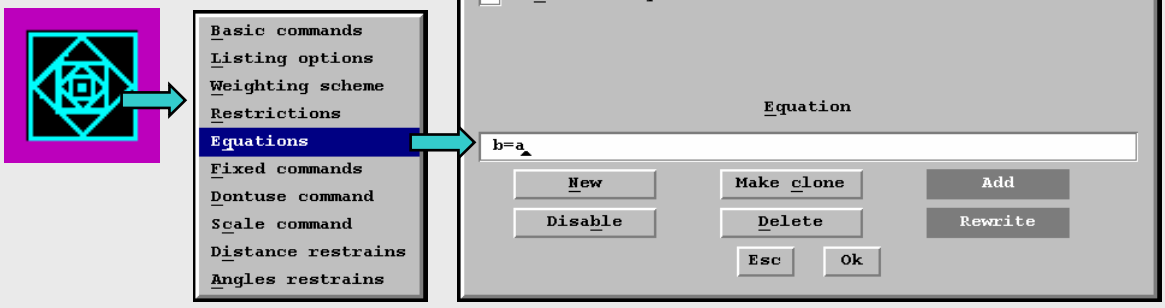
[1] GV is not applicable for synchrotron radiation.

[2] To get more space on the screen we can disable plotting of the difference curve through *Options*.

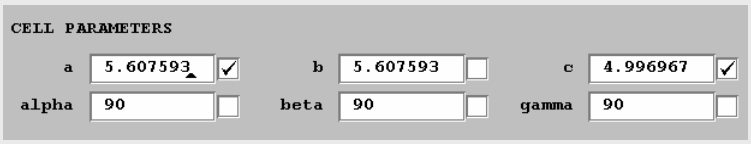
[3] Full Width in Half Maximum

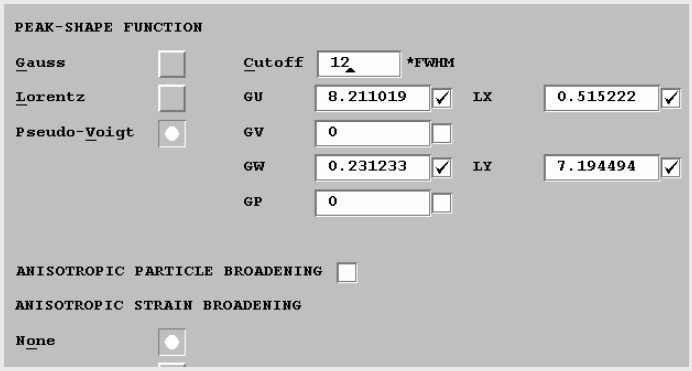
Refinement of basic profile parameters of PbO

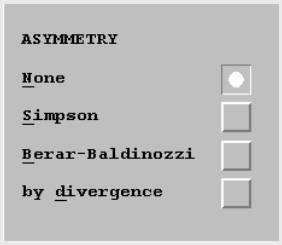
Binding *a* with *b* in a pseudo-tetragonal structure

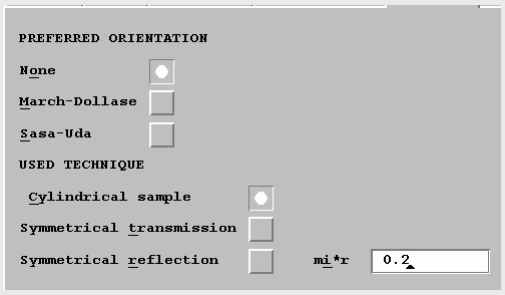


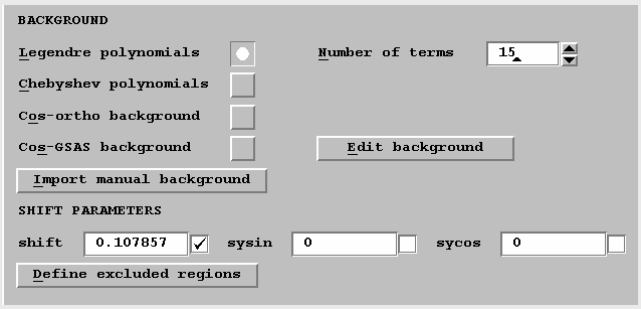
Profile parameters of the basic profile

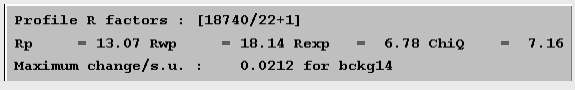




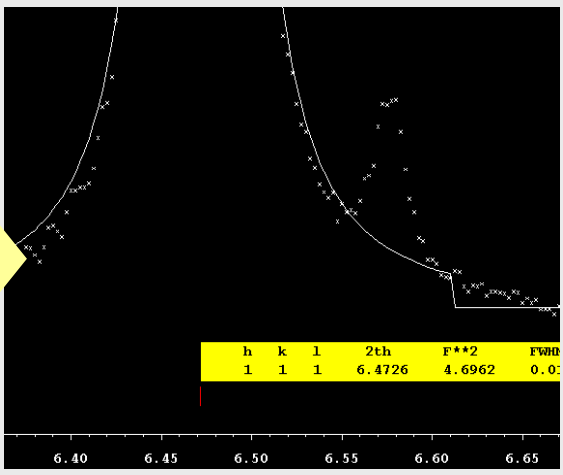








The cutoff of 8 FWHM is not sufficient for some strong reflections



1.6.1.2 Anisotropic strain broadening

An inspection of the profile in the *Profile viewer* reveals that a strong broadening occurs in the sample, that is clearly visible e.g. for the reflection *2 2 0* at 2θ=10.15º. On the other hand, some calculated profiles are too wide, for instance the one for *0 4 0* at 2θ=14.37º. To correct for this phenomenon the *Anisotropic strain broadening* should be refined by the tensor method.

The tensor components should be restricted according to the lattice symmetry but the automatic restrictions are based on the orthorhombic symmetry. To simulate the pseudo tetragonal symmetry we must define equations *St040=St400* and *St022=St220*.

At the beginning, we only allow refinement of *St220*. It will converge with $R_p \approx$ 10%. Then we allow refinement of all *St* components. *Refine* will fix all components that must be fixed in the orthorhombic crystal and it will apply the equations, too. The refinement will show strong oscillations of some *St* components without large impact on the R_p value.

1.6.1.3 Profile asymmetry

Besides the strain broadening, the profile is also affected by the profile asymmetry that is perspicuous for instance for the reflection *0 0 1* at 2θ=4.02º. For the asymmetry correction, we shall use the *divergence method* withs two refinble parameters *S/L* and *H/L*. In the given experimental arrangement it is reasonable to use the equation *H/L=2*S/L*. The refinement will converge at $R_p \approx$ 9%. The problems with oscillating *St* components remain but we shall solve them later during the structure refinement.

1.6.2 Average structure

With refined profile parameters, we can call the external program *EXPO* [2] for solution of the structure by direct methods. In the next scheme, we should check if the coordinates returned by *EXPO* are consistent with the ones given in this manual. Then we refine the average structure with isotropic ADP for both atoms and finally we use harmonic ADP for lead. The *U22* component will be significantly larger than *U11* and *U33*. The R_p factor at this stage is about 10% and the *R* factor is 4.5%.

This structure model breaks the pseudo tetragonal character of our refinement. We can therefore delete all related equations, i.e. *a=b*, *St040=St400* and *St022=St220*. Then we enable refinement of all cell parameters and of all *St* components (that will then be automatically restricted by the orthorhombic symmetry) and we start refinement with damping factor 0.5. After many cycles, the *R* and R_p factors will be about 3.7% and 8.7%, respectively, and *St040* will strongly oscillate.

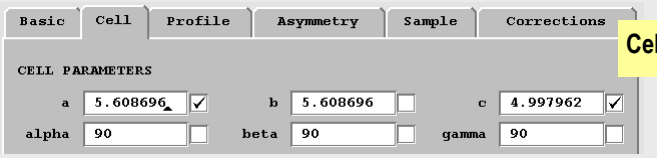
In the refinement listing, we can see that only *St400*, *St220* and *St004* are strongly above the three sigma limit. We shall fix the remaining *St* components and continue refinement that will finish with $R_p \approx$ 8.7%, $R \approx$ 3.7% and slightly oscilating *Shift* and cell parameters.

Average structure of PbO

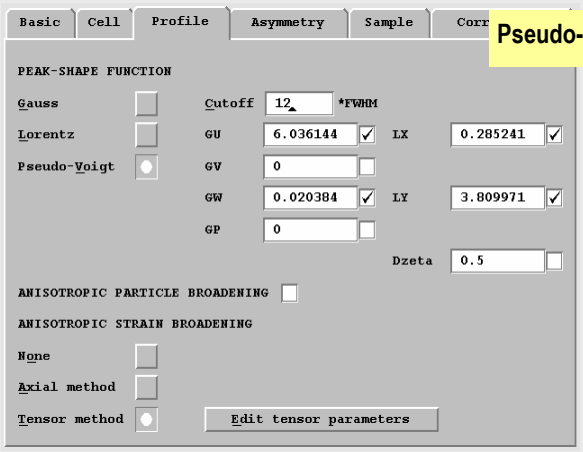
1. Refinement with pseudo-tetragonal restrictions

Equations in 50

```
equation : b=a
equation : St040=St400
equation : St022=St220
equation : h/l=2*s/l
```

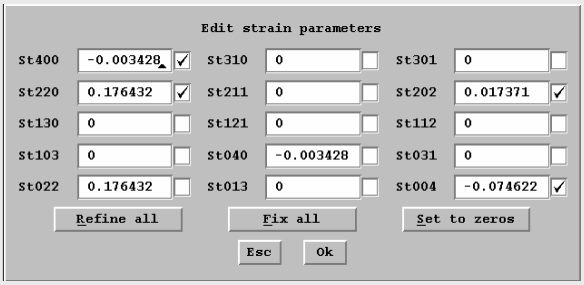


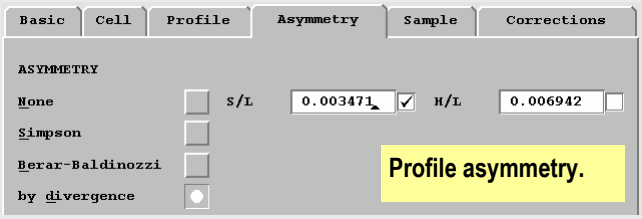
Cell parameters; a=b



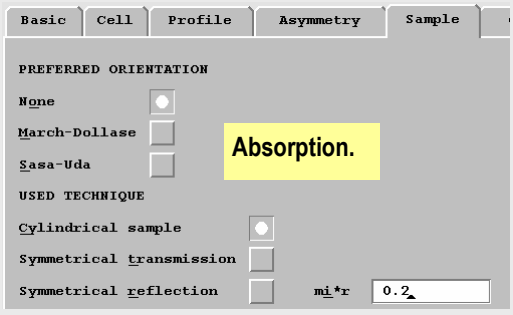
Pseudo-Voigt profile.

Anisotropic strain broadening.
St040=St400; St022=St220

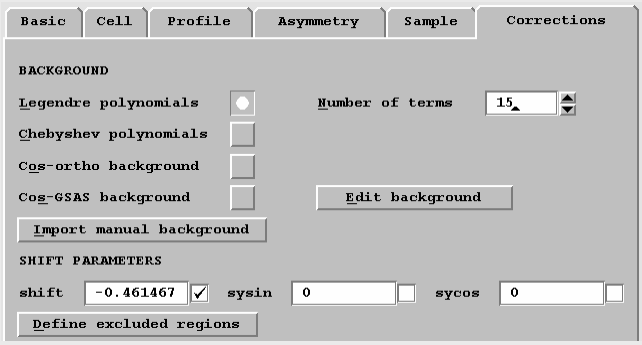




Profile asymmetry.



Absorption.



Background and shift corrections.

```
    2    0    0    0
 0.015888 0.000000 0.000000 0.000000 0.000000 0.000000       100000
 0.000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000       000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000       000000
Pb1        1  2     0.250000 0.000000 0.250000 0.737329
 0.001197 0.019425 0.005458 0.000000 0.000000 0.000000       0001111000
O1         2  1     0.250000 0.750000 0.000000 0.500000
 0.004807 0.000000 0.000000 0.000000 0.000000 0.000000       0000100000
```

Average structure after refiement with tetragonal cell parameters.

Average structure of PbO

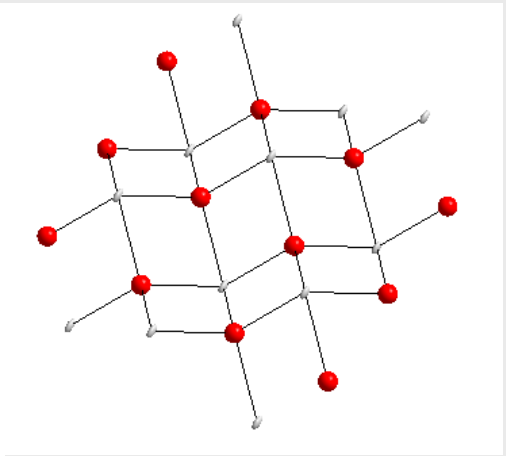
2. Refinement without pseudo-tetragonal restrictions

```
!equation : b=a
!equation : St040=St400
!equation : St022=St220
equation : h/l=2*s/l
```

Equations in 50

R values

```
Overall R factors : [578=440+138/6]
R(obs) =  3.66 Rw(obs) =  2.03 R(all) =  4.51 Rw(all) =  2.04
Profile R factors : [18740/27+6]
Rp     =  8.67 Rwp     = 11.32 Rexp    =  6.77 ChiQ     =  2.79
Maximum change/s.u. :    0.8652 for shift
```



```
   2    0    0    0
 0.015878 0.000000 0.000000 0.000000 0.000000 0.000000       100000
 0.000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000       000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000       000000
Pb1       1  2     0.250000 0.000000 0.250000 0.737323
 0.003688 0.014401 0.005586 0.000000 0.000000 0.000000      0001111000
O1        2  1     0.250000 0.750000 0.000000 0.500000
 0.003111 0.000000 0.000000 0.000000 0.000000 0.000000      0000100000
```

Average structure after refiement with orthorhombic cell parameters

Basic | Cell | Profile | Asymmetry | Sample | Corrections

CELL PARAMETERS

a	5.607601	b	5.610209	c	4.998065
alpha	90	beta	90	gamma	90

Basic | Cell | Profile | Asymmetry | Sample | Corrections

PEAK-SHAPE FUNCTION

Gauss		Cutoff	12 *FWHM		
Lorentz		GU	-4.043073	LX	0.27353
Pseudo-Voigt	●	GV	0		
		GW	0.038504	LY	4.295746
		GP	0		

Edit strain parameters

St400	0.009074	St310	0	St301	0
St220	0.284919	St211	0	St202	0
St130	0	St121	0	St112	0
St103	0	St040	0	St031	0
St022	0	St013	0	St004	0.131451

Refine all | Fix all | Set to zeros

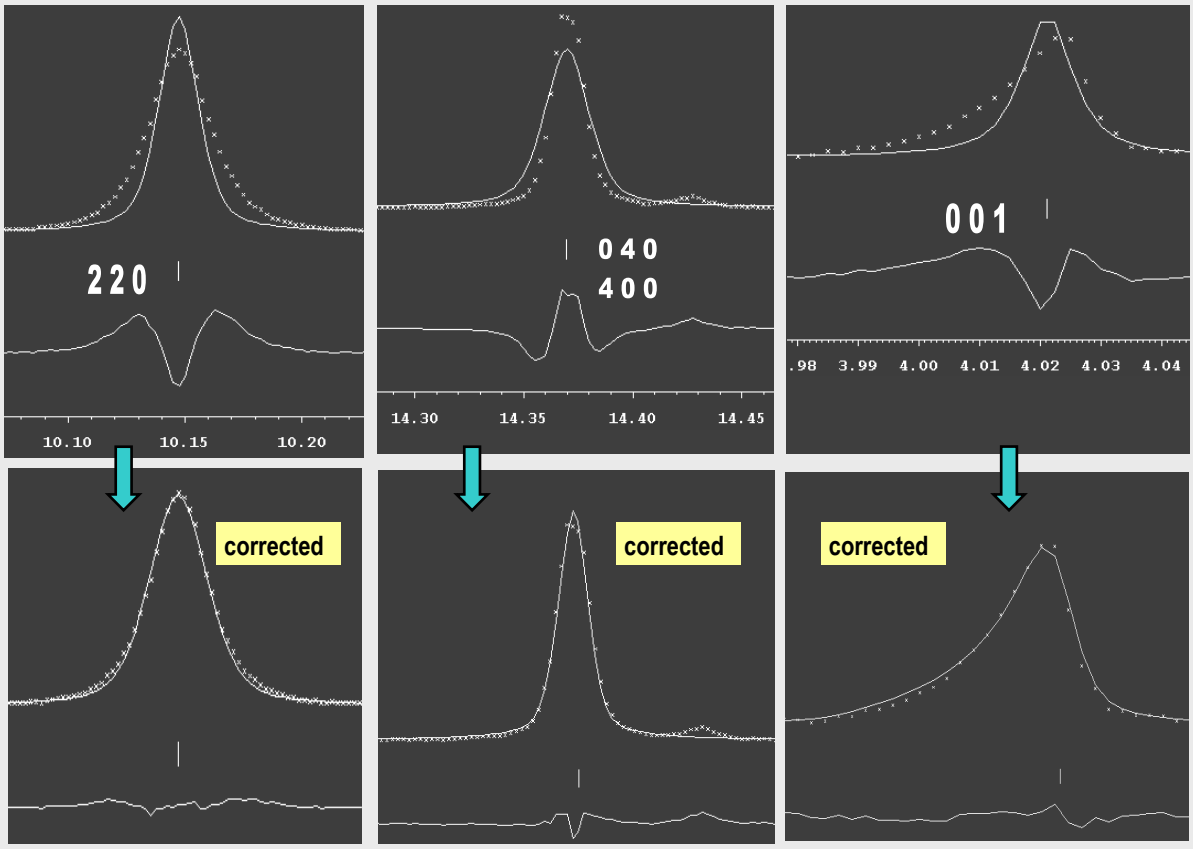
Esc | Ok

SHIFT PARAMETERS

shift -0.492575 sysin 0

Define excluded regions

An influence of the correction for anisotropic strain broadening and asymmetry on selected peaks.



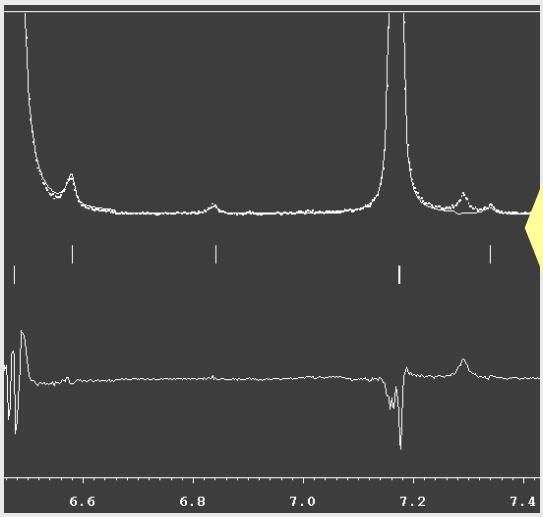
1.6.3 Adding the second phase

In the *Profile viewer*, little unassigned peaks indicate an admixture of another phase. In order to filter out its influence we add this phase by *Tools →Powder →New Phase* using the information given in the table at the beginning of this chapter, page 95. Both the basic crystal information and the structure itself must be defined using *EditM50* and *EditM40*. We shall use label *b* for the second phase and change the default label *Phase#1* of the first phase to *a*.

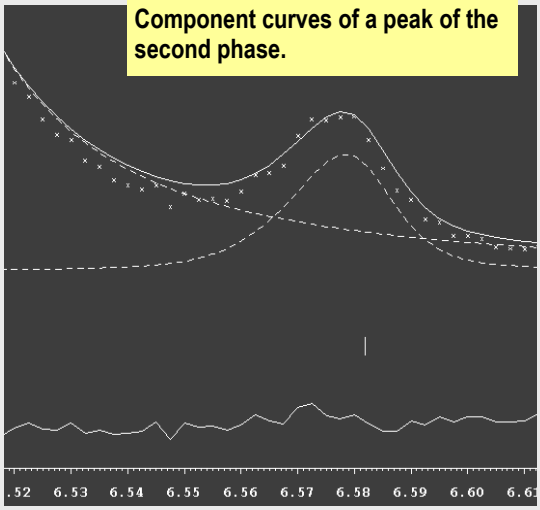
The second phase inherits the profile parameters of the first one except the *Strain broadening* parameters. By default, only the background and shift parameters can be refined as they are common to both phases; the others are fixed. As the admixture of the second phase is very small, its structure cannot be refined. It must be fixed by the *Fixed command*. In our example, we are using names *Pb1_b* and *O1_b* in the second phase so that we can use a wildcard and fix coordinates of the atoms **_b*. The isotropic ADP of the second phase must restricted to be the same by *Restrictions* in the Refinement commands in order to avoid negative values.

We still use damping 0.5. At the beginning, we refine only common profile parameters, i.e. *Shift* and background. Then we refine cell parameter and the volume fraction (see *Parameters →Scale/twin*) and finaly we refine also *GW* and *LX*. Refinement of all pseudo-Voigt parameters is not possible. The final R-values are R_{obs}≈8.7% and R_p≈8.5%. By using *Details* in the *Profile viewer* we can see the peaks of the second phase are described relatively well.

Adding the second phase of PbO



The profile plot after refinement with the second phase. Note that some small peaks are still not described.



Component curves of a peak of the second phase.

M40 with two phases.

```
   2    0    0    0
   2    0    0    0
 0.015958 0.000000 0.000000 0.000000 0.000000 0.011774
 0.000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
Pb1       1  2     0.250000 0.000000 0.250000 0.737309
 0.003579 0.014384 0.005504 0.000000 0.000000 0.000000
O1        2  1     0.250000 0.750000 0.000000 0.500000
 0.003655 0.000000 0.000000 0.000000 0.000000 0.000000
Pb1_b     1  1     0.500000-0.020800 0.250000 0.230900
 0.008525 0.000000 0.000000 0.000000 0.000000 0.000000
O1_b      2  1     0.500000 0.088600 0.250000-0.130900
 0.008525 0.000000 0.000000 0.000000 0.000000 0.000000
```

```
Overall R factors for a : [578=446+132/6]
R(obs) =  3.60 Rw(obs) =  2.96 R(all) =  4.40 Rw(all) =  2.97
Overall R factors for b : [1058=516+542/2]
R(obs) =  8.66 Rw(obs) =  3.76 R(all) = 13.18 Rw(all) =  3.93
Profile R factors : [18740/32+8]
Rp     =  8.46 Rwp     = 10.73 Rexp   =  6.77 ChiQ    =  2.51
Maximum change/s.u. :    0.1479 for shift
```

1.6.4 Refinement of modulated structure

In the profile viewer, we can see some peaks are still unassigned. They are satellites of the first phase. In the next step, we shall introduce and refine modulated structure.

Unlike a single crystal structure, the number of dimensions in *EditM50* can be edited any time. We change it to four and define **q** vector and the superspace symmetry. Then in *Powder options* for phase *a* we set the maximal satellite symbol to one.

In *EditM40* we set one position modulation wave for Pb1 and refine with damping 0.1 that can be changed after several cycles to 0.5. Then we allow refinement of **q** vector and refine one position modulation wave for oxygen. After many cycles, we can see in the refinement listing that the parameters *St400* of the first phase and *LX* of the second phase are below the three-sigma limit. We set them to zero and disable their refinement. The isotropic ADP of O1 will be probably negative. We shall fix it to the value 0.005 and continue refinement. The results are listed in the next scheme.

Modulated structure: the final model

M40

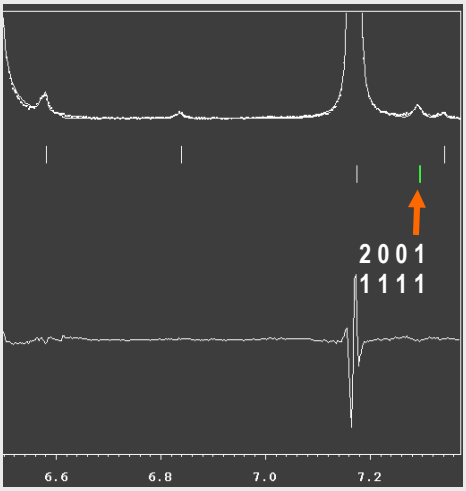
```
   2    0    0    0
   2    0    0    0
 0.015937 0.000000 0.000000 0.000000 0.000000 0.009176      100001
 0.000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000      000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000      000000
Pb1       1  2     0.250000 0.000000 0.250000 0.737216      000  0  1  0
 0.007070 0.005138 0.005836 0.000000 0.000000 0.000000      0001111000
 0.018004 0.000000 0.000000 0.000000 0.000000 0.000000      100000
 0.000000                                                   0
O1        2  1     0.250000 0.750000 0.000000 0.500000      000  0  1  0
 0.005000 0.000000 0.000000 0.000000 0.000000 0.000000      0000000000
 0.020036 0.000000 0.000000 0.000000 0.000000 0.027253      100001
 0.000000                                                   0
Pb1_b     1  1     0.500000-0.020800 0.250000 0.230900
 0.007022 0.000000 0.000000 0.000000 0.000000 0.000000      0000100000
O1_b      2  1     0.500000 0.088600 0.250000-0.130900
 0.007022 0.000000 0.000000 0.000000 0.000000 0.000000      0000000000
```

```
Overall R factors : [1530=1158+372/8]
R(obs) =  3.12 Rw(obs) =  2.39 R(all) =  3.89 Rw(all) =  2.40
R factors for main reflections : [578=466+112]
R(obs) =  2.65 Rw(obs) =  2.33 R(all) =  3.29 Rw(all) =  2.34
R factors for satellites of order 1 : [952=692+260]
R(obs) =  4.42 Rw(obs) =  2.56 R(all) =  5.33 Rw(all) =  2.61
Profile R factors : [18740/31+10]
Rp     =  7.50 Rwp     =  8.73 Rexp   =  6.77 ChiQ    =  1.66
Maximum change/s.u. :    0.2856 for b[a]
```

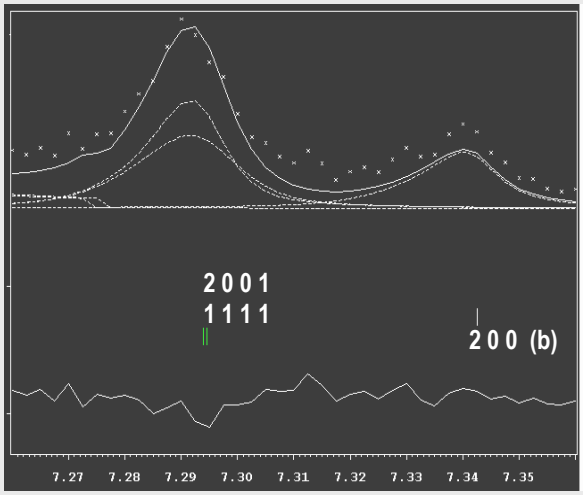
Refinement results for phase “a” and “b”

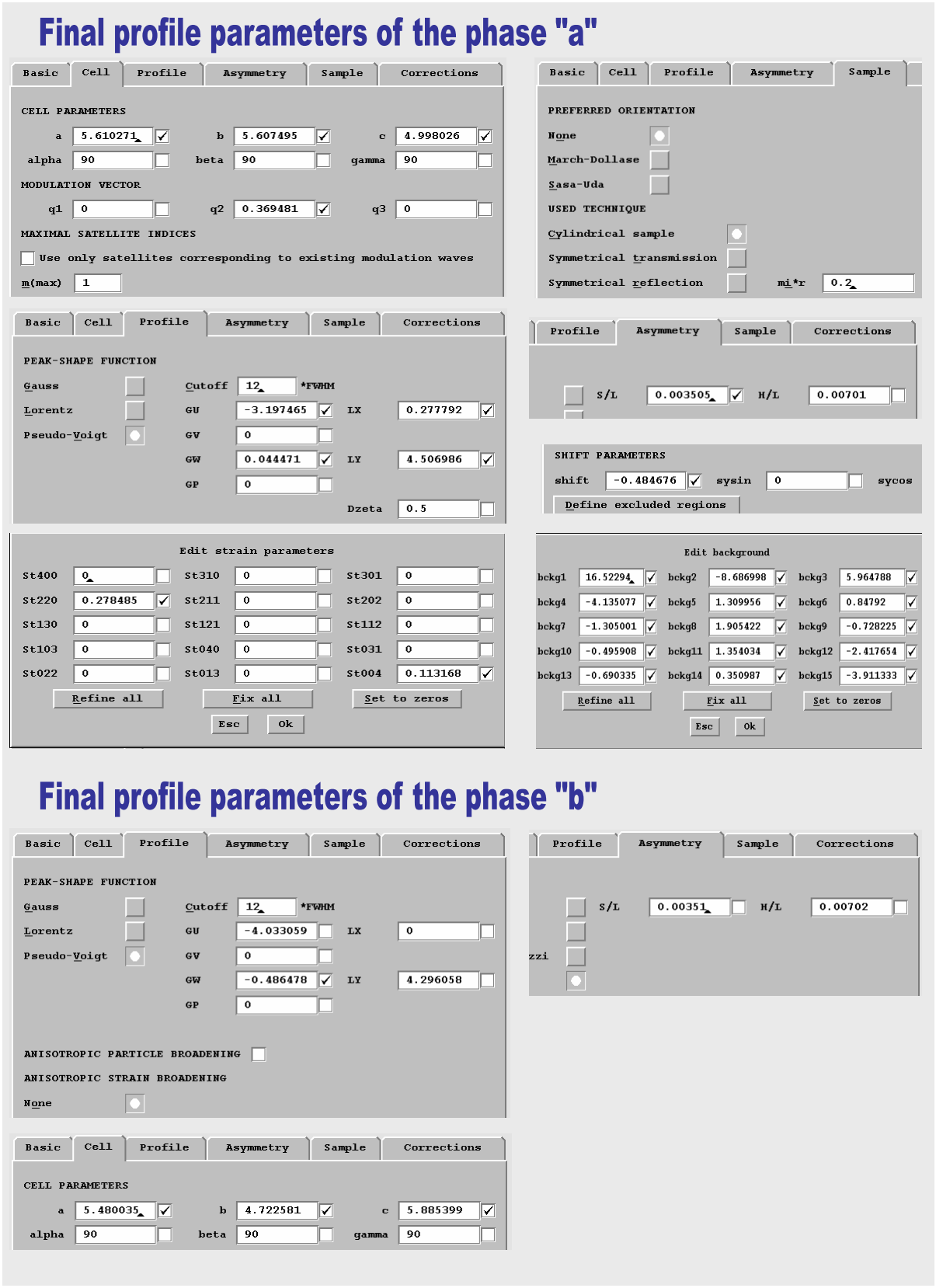
```
Overall R factors for a : [1530=1159+371/8]
R(obs) =  3.13 Rw(obs) =  2.39 R(all) =  3.89 Rw(all) =  2.41
Overall R factors for b : [1059=601+458/2]
R(obs) =  6.38 Rw(obs) =  2.87 R(all) =  8.60 Rw(all) =  3.01
Profile R factors : [18740/31+10]
Rp     =  7.51 Rwp     =  8.73 Rexp   =  6.77 ChiQ    =  1.66
```

An example of satellite peak



Fit of satellite reflections in the profile plot

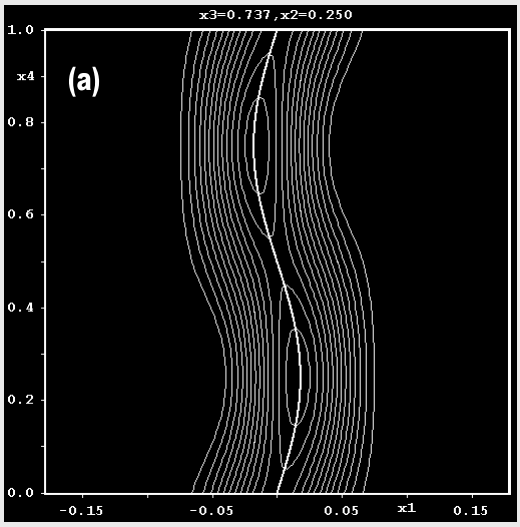




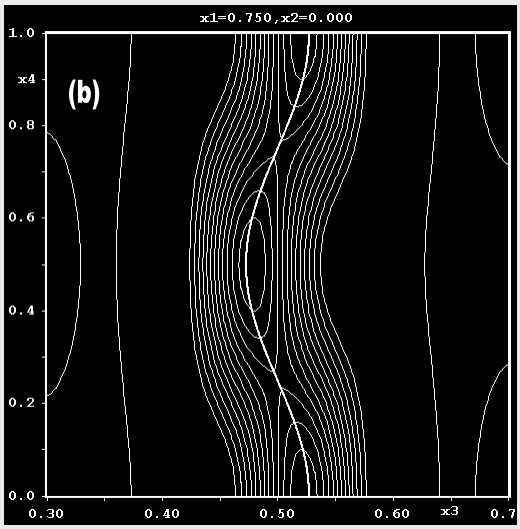
The profile parameters listed in this scheme have only orientational meaning as one could get the same profile fit using different profile parameters. It is especially true for the second phase. The refinement of profile parameters influences the isotropic ADP of oxygen and of both atoms of the second phase. On the other hand, the most pronounced features of the structure are reliably estimated. It is especially larger *U22* component of the harmonic ADP of the lead that becomes comparable with *U11* and *U33* after refinement of positional modulation.

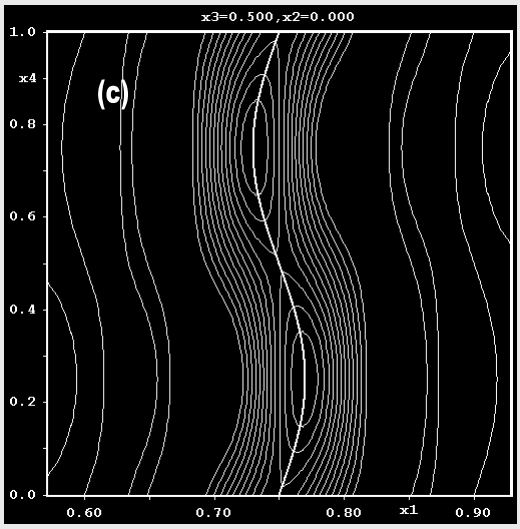
The plots of modulation functions in the next scheme show the functions are well described. The atomic domain of oxygen shows some discontinuity that could be probably better described with crenel functions but this is far beyond resolution of this experiment.

Modulation functions in the phase "a"



(a) x1-x4 section through the Pb1 position, contour step 100e·A^{-3}
(b) x3-x4 section through theO1 position, contour step 5e·A^{-3}
(c) x1-x4 section through theO1 position, contour step 5e·A^{-3}





References

[1] Altomare, A., Burla, M.C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A.G.G., Polidori, G. and Spagna, R. (1997). SIR97, program for solving and refining crystal structures. http://www.irmec.ba.cnr.it/

[2] Altomare, A., Burla, M.C., Carrozzini, B., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A.G.G., Polidori, G. and Rizzi, R. (1999). EXPO, program for solving crystal structures from powder diffraction data. **http://www.irmec.ba.cnr.it/**

[3] DIAMOND - Visual Crystal Structure Information System. J.Appl.Cryst (1999), 32, 1028-1029.

[4] Dusek, M., Slouf, M. (2002). Unpublished results.

[5] Dusek, M., Petricek, V., Wunschel, M., Dinnebier, R.E. and Smaalen, S. van (2001). J.Appl.Cryst. **34**, 398-404. Refinement of modulated structures against X-ray powder diffraction data with Jana2000.

[6] Danielson, E., Devenney, M., Giaquinta, D.M., Golden, J.H., Haushalter, R.C., McFarland, E.W., Poojary, D.M., Reaves, C.M., Weinberg, W.H. & Wu, X.D. (1998). Journal of Molecular Structure, **470**, 229-235. X-ray powder structure of Sr_2CeO_4 : a new luminescent material discovered by combinatorial chemistry.

[7] Dusek, M., Chapuis, G., Meyer,M. & Petricek,V.(2003). Acta Cryst **B59**, 337-352. Sodium carbonate revisited.

[8] Van Smaalen, S. and Bronsema, K.D. (1986). Acta Cryst. **B42**,43-50. The determination of the incommensurately modulated structure of niobium tetratelluride.

[9] Unpublished measurement.

[10] Nye, A. (1992). Xlib Programming manual for version 11, Third Edition. O'Reilly & Associates, Inc.

[11] http://www.rarlab.com/index.htm

[12] http://www.lahey.com/

[13] http://www.winteracter.com/

A Installation

Jana2000 is freely available in the **Jana2000 homepage**[1] or in the **anonymous ftp**[2] server. The following files can be downloaded:

README.TXT	Downloading and installation notes
jana2000Pack.exe	The self extracting installation file for UNIX
jana2000.tar.gz	Installation files for UNIX compressed by gzip
janainst.exe	Files for Windows containing the executable optimized for Intel Pentium Pro, Pentium II, Pentium III and compatible processors.3
manual2000.pdf **manual2000.doc**	this manual

For UNIX the recommended way of installation is to process jana2000Pack.exe[4] by command

```
source jana2000Pack.exe
```

executed from the prompt of *csh* or *tcsh*.
For Windows the installation is started by executing janainst.exe.

A.1 Ftp commands

Jana2000 is usually downloaded through the WWW. An alternative way is downloading by ftp from the anonymous ftp server ftp.fzu.cz. Besides various graphical ftp programs a command line ftp exists that can be usually started from the prompt in UNIX workstation or through *Start* → *Run* under Windows. Here are ftp command necessary for downloading of *Jana2000*:

Command	Meaning
ftp ftp.fzu.cz	Connects to the server ftp.fzu.cz. The user name is "anonymous", the password is the e-mail address of the user.
cd pub/cryst/jana2000	Changes remote directory to jana2000
lcd c:\something	Changes local directory (important for Windows where it is not sure what is the default local directory)
dir	Shows contents of the remote directory
binary	Sets binary transfer
get janainst.exe	Copies the installation file from the remote directory to the local directory.
quit	Exits ftp

A.2 Installation of UNIX version

A.2.1 Installation from jana2000Pack.exe

The distribution contains source files and *Makefile* for the basic UNIX platforms: *SunOS/Solaris, IRIX, HPUX, AIX, LINUX, OSF* and *MACOSX*. For successful compilation compilers of the *C* and *FORTRAN77* or *FORTRAN90* languages and X11 graphical library [10] are necessary.

---

[1] http://www-xray.fzu.cz/jana/jana.html
[2] ftp://ftp.fzu.cz/pub/cryst
[3] Versions for older processors, for instance 486, will be delivered by request.
[4] The extension *exe* is used in order to convince Web browsers that it is a binary file. In fact the file is not executable. It is combination of an ASCII header and a binary archive.

The installation is started by command

```
source jana2000Pack.exe
```

from *csh* or *tcsh* shell. In case of other shells (*sh,bash, ksh* etc.) csh must be started beforehand:

```
csh                          starts csh
source jana2000Pack.exe      starts automatic installation
exit                         exits csh
```

The installation procedure creates the directory jana2000 and extracts all files to this directory. Then it detects type of UNIX workstation and activates (by removing comments) the relevant part of the *Makefile*. In the next step, it runs a testing compilation of a small program that uses X11 library and in case of troubles it attempts to find a proper path to X11 include files and X11 library. Finally, it starts the compilation of *JANA2000*.

A.2.2 Installation from jana2000.tar.gz

Sometimes the compilation requires special settings that are not available in the distributed *Makefile*. In such case, *Jana2000* can be installed manually from the file jana2000.tar.gz. Here are the instructions:

Command	Meaning
gunzip jana2000.tar.gz	Replaces the compressed file jana2000.tar.gz with the uncompressed jana2000.tar.
tar xf jana2000.tar	Creates directory jana2000 and extracts here all files from the archive jana2000.tar. The files of the same name will be overwritten without any warning. The resulting directory structure is ./jana2000/source ./jana2000/source/fg ./jana2000/source/data ./jana2000/test
	The directory jana2000 contains the Makefile – the description file for the compilation tool *make*. The directories `source', `data' and `fg' contain the source files. The testing examples are in the directory `test'.
cd jana2000	Changes directory to jana2000.
edit Makefile	Makefile must be edited before the compilation. Find editable section corresponding to your computer and compiler, remove "#" from the first column and save it.
make	Executes commands from the Makefile. Builds the libraries and compiles all programs of the package.
make clean_up	Removes object files, libraries and temporary files. This command is optional.
cd test	Changes directory to testing examples
../jana2000 testa	Runs a testing example

A.2.3 Directory structure of UNIX version

The following scheme shows directory structure of *Jana2000* for UNIX after extraction from jana2000Pack.exe or jana2000.tar and compilation. Directories d and specific are created by make and are only needed for compilation. Directories source and source/fg contain complete source code of *Jana2000*. Directory source/data contains postscript header files for printing of Jana listing, icon images, bond valence parameters, CIF dictionary and atomic form factors. Directory test contains example structures for testing refinements.

The directories source/data and source/fg must be accessible by the program in the run time (see *JANADIR*).

A.2.4 The environmental variable JANADIR

Jana2000 uses various files from directories source/fg and source/data. The compiled program remembers the path to the installation directory (usually jana2000) and expects the directory source is its subdirectory. The installed program can be used without setting of *JANADIR* only if (1) the variable is undefined; (2) the directory *source* is in the same place as it was in the compilation time.

In case of post compilation changes, for instance when moving *jana2000* to usr/bin, usr/local/bin etc., *JANADIR* must be redefined.

- The compiled program can be moved to an arbitrary place without setting of *JANADIR* if the directory source remains in the same place like in the compilation time.
- If *JANADIR* is set it must point one level above the directory source.

Commands to set JANADIR:

csh or tcsh `setenv JANADIR my_path`
sh or bash `set JANADIR=my_path; export JANADIR`

Startup files .cshrc, .tcshrc or .bashrc in the user's root directory can be used for automatic definition of *JANADIR* when the relevant shell is started.

A.2.5 Adjustable parameters

The program is written in FORTRAN77[1] that cannot allocate memory dynamically. This means that the maximal number of atoms, molecules etc. in *Jana2000* is fixed in the compilation time.

Users of UNIX version can change many of these limits in file source/params.cmn. Then the program must be recompiled by command *make* executed in the directory *JANADIR*. For Windows version, it is not possible as the program is distributed as precompiled binary file. A compiled program for Windows with changed limits can be obtained from the authors by request.

Proper behavior of the programs after changing any limit is not guaranteed. Increasing the parameters is usually safe. Lowering is more complicated as it affects size of temporary field *scrar* used by the program for various purposes.

[1] The reason we do not use FORTRAN90 or 95 is that no such compiler is publicly available in LINUX computers.

Adjustable parameters in params.cmn

Name of parameter	Description
MXA	Number of atoms
MXM	Number of molecules
MXP	Number of the positions of a single molecule
MXW	Number of modulation waves
MXPG	Number of pages of listing
MXO	?
MXLINE	Number of lines in the page of listing
MXREF	Number of the reflections for the refinement
MXTBL	Size of Fourier map
MXSYM	?
MXCEN	Number of centering vectors
MXFACE	Number of faces of crystal shape
MXDA	?
MXDM	?
MXGP	?
MXPHASES	Number of phases in multiphase refinement
MXBACKG	Number of background parameters
NPARPWD	Number of profile parameters ?
NMAXDRAW	?
IMAX	Maximal integer ?
MXPNTS	Number of points in powder profile
MXE	Number of equations in m50
MXEP	Number of parameters in single equation
MXPARRF	Number of refined parameters

File params.cmn (version 22/04/2003)

```
      parameter (mxa=500,mxm=10,mxp=15,mxw=32,mxpg=120,mxo=40,mxline=55,
     1           mxref=400000,mxtbl=200000,mxsym=1920,mxcen=32,
     2           mxface=32,mxw21=1+2*mxw,mxda=100,mxdm=100,mxgp=100,
     3           MxPhases=5,MxBackg=36,NParPwd=100,NMaxDraw=2000,
     4           MxParPwd=MxBackg+3+MxPhases*NParPwd,imax=2147483647,
     5           mxsup=mxa*mxgp,mxwq=mxw21*mxw21,mxpnts=30000,
     6           ndoffpwd=18*(1+2*(6+15)),ndoff=ndoffpwd+MxParPwd,
     7           mxe=500,mxep=100,npmp=ndoff+2*mxa*mxda+1,
     8           mxder=npmp+mxdm*mxp*mxm-1,mxparrf=2000,
     9           matice=(mxparrf+1)*mxparrf/2,
     a           mxscr=matice+7*mxder+mxsup*(16+2*mxw),
     1           mxdam=84*(1+2*mxw)+3+68,mxdmm=30+56*mxw)
```

A.2.6 Speed of UNIX version

Speed of *Jana2000* for interactive work can be best estimated visually by opening and closing pull-down menus and submenus. It should be as fast as the Windows version in a comparable PC. Sometimes the user is connected to a UNIX workstation from some local computer using the network. If the speed of the network connection is 10Mbps or more and the line is not overloaded, the interaction should be almost as fast as without network. However, the speed of graphics can be significantly degraded by using the *secure shell (ssh)*.

When we log in a UNIX server with *ssh* the connection is redirected through a secure encrypted channel. The X11 graphics is forwarded through a secure channel, too.

This significantly slows down the performance of interactive jobs like listing through pull-down menus. The interactive job may be **very slow** even with fast UNIX workstation and fast X11 server. We suggest the following solution:

- ***Check whether your graphics is encrypted.*** This can be done by displaying your display address by command `echo $DISPLAY`. Secure display address looks like *xxxx:n.0* , where *xxxx* is the name of the Unix workstation you are connected to and *n* is usually greater than nine. Non-secure display address looks like *yyyy:0* , where *yyyy* is the name of the local terminal you are connected from.
- ***Change the display address to a non-secure form***. This is done by command (under the *C-shell*) `setenv DISPLAY yyyy:0` , where *yyyy* is name of the local terminal. After this all graphical applications started from this terminal window will use the non-encrypted connection for graphics.

For changing the display only for *Jana2000* but not for the other applications started from the same terminal we can use command
`(setenv DISPLAY yyyy:0; jana2000)&`
The brackets cause the command runs in a separate shell and the DISPLAY setting for the terminal window remains unchanged.

A.3 Installation of Windows version

A.3.1 Installation from janainst.exe

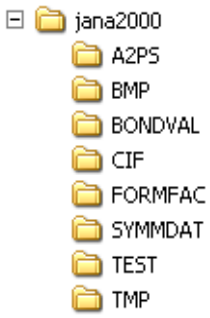
The PC version is distributed as a self-extracting installation file compressed by *Rar* [10]. It contains the compiled program jana2000.exe and all other necessary files. The source code is not included. The program is compiled by LF95 [12] and the graphic interface is based on WINTERACTER [13]. Here are the installation instructions:

- Run janainst.exe. It will prompt for information where to extract the files. The standard path is c:\jana2000 or c:\Program Files\jana2000.
- Set the environment variable *JANADIR* to contain the directory where *Jana2000* has been installed.
- In case of Windows NT/2000/XP set the full access for everybody to the directory *JANADIR*.
- Add jana2000.exe to the path or create an icon for calling *Jana2000* or associate typical extensions of Jana files (M40, M50 …) with jana2000.exe.
- Run the testing examples in the *JANADIR*\test directory.

A.3.2 Directory structure of Windows version

The following scheme shows directory structure of Jana2000 for Windows after extraction from the installation file. A2ps contains postscript header files for printing of Jana listing. Bmp contains icons. Bondval contains bond valence parameters. Cif contains the CIF dictionary. Formfac contains atomic form factors. Symmdat contains space group information, Test contains example structures for testing refinements and Tmp is temporary space[1].

[1] Can be redefined in Tools →Preferences.



A.3.3 Setting of *JANADIR* and *PATH*

Jana2000 for Windows requires the environment variable *JANADIR* to be set to the directory containing jana2000.exe. The directories A2PS, BMP etc. must be subdirectories of *JANADIR*.

Windows95/98/ME

The environment variables are defined in c:\autoexec.bat. They are active after reboot of the computer. The relevant lines for *JANA2000* installed in C:\jana2000 directory are

```
set JANADIR=C:\jana2000
set PATH=%PATH%;c:\jana2000;
```

The second command means the path to Jana2000 is appended to an existing PATH. Both commands are case insensitive.

WindowsNT/2000/XP

These systems establish two kinds of environment variables:
The ***system environment variables*** are the same no matter who is logged on at the computer. They can be changed by members of the Administrators group. The ***user environment variables*** can be different for each user of a particular computer. After change any environment variables, Windows 2000 saves the new values in the registry, making them automatically available the next time you start your computer. Environment variables are set in the following order:

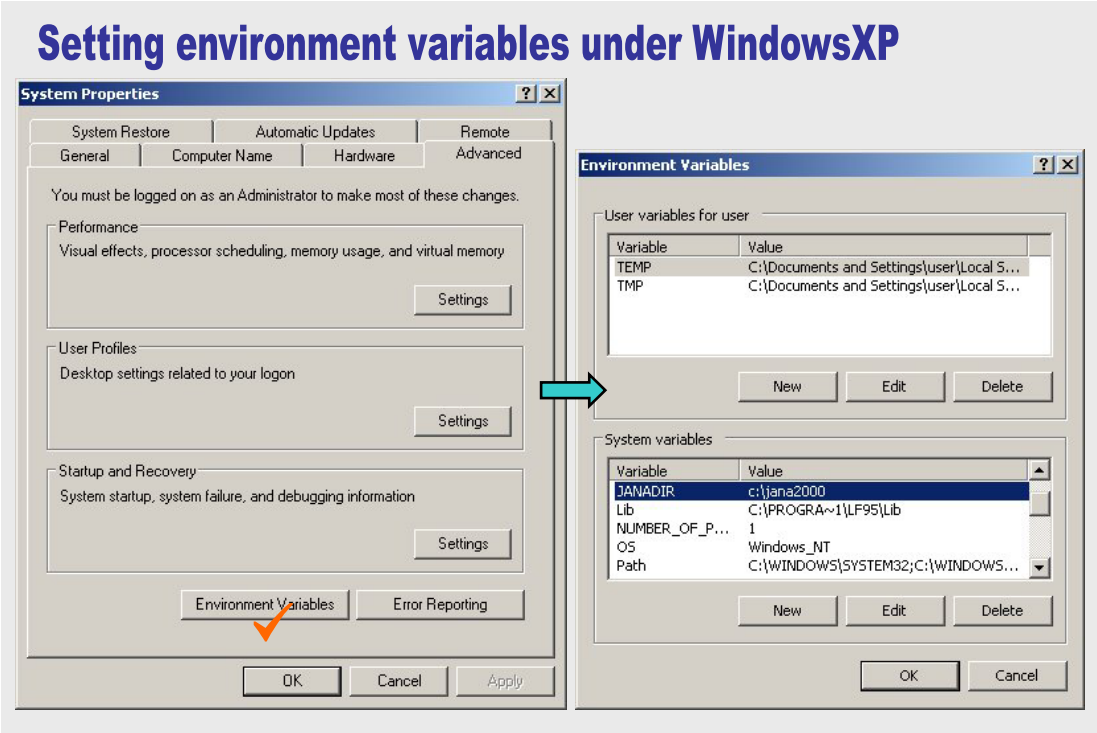
- System variables
- AUTOEXEC.BAT[1] variables
- User variables

The variables of the same name are overwritten. Unlike in UNIX systems the names of environment variables are case insensitive. The PATH variable is built in slightly different way: the User path is appended to the system path and then the path from the AUTOEXEC.BAT file is appended.

Setting of environmental variables differs for various kinds of Windows:

Windows NT	Start → Setting → Control Panel → System → Environment
Windows2000	Start → Setting → Control Panel → Advanced → Environment variables
WindowsXP	Start → Setting → Control Panel → System → Advanced → Environment variables

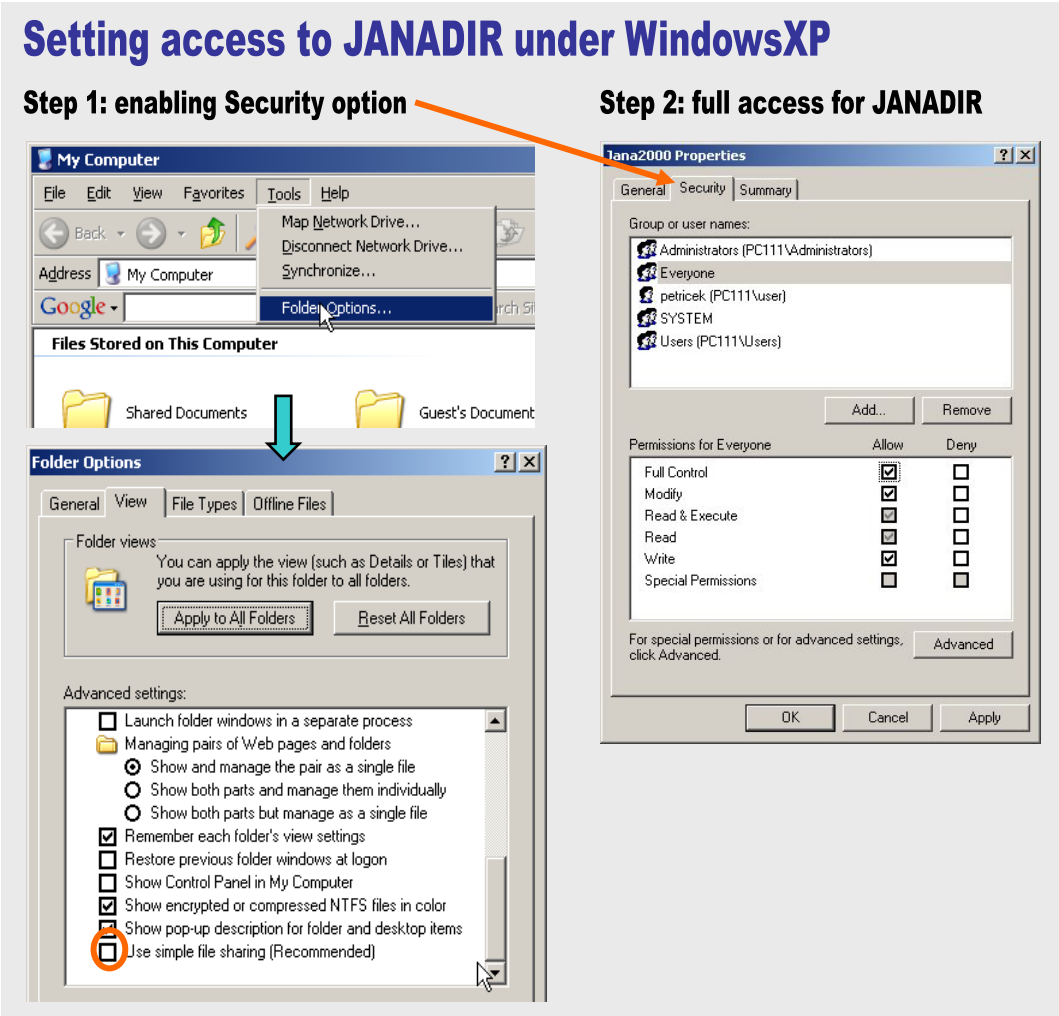
[1] MSDOS or 16-bit Windows applications running under WindowsNT/2000/XP do not read autoexec.bat. They read autoexec.nt instead. *JANADIR* should not be defined neither in autoexec.nt nor in autoexec.bat.



A.3.4 Security setting under WindowsXP

In WindowsNT/2000/XP only *Administrators* have write permission to all files. The permissions of the other users are limited. Jana2000 is usually installed by Administrator but it needs the write access to some files in jana2000 directory[1] also in the run time when it may be executed by ordinary users or by *Guest*. The access to files can be defined by Right-clicking on the file/directory name in *My Computer* and by choosing *Properties* → *Security*. The easiest way is to set the full access for *Everyone* for directory jana2000. The *Security* subwindow is only visible if the *Simple file sharing* is disabled.

[1] In UNIX version, every user has a root directory and the files (for instance jana2000.ini) are placed there. In Windows, the root directories do not exist and this is why Jana2000 is still installed like for one user PC.



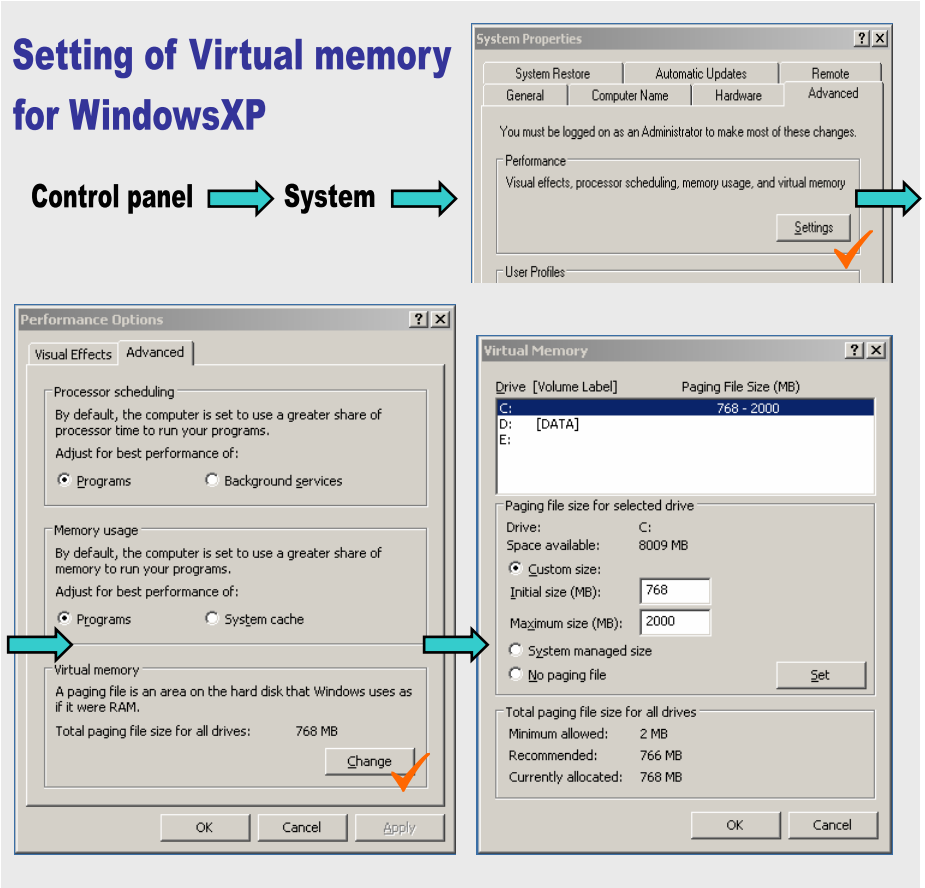
In the run time, the path to the root directory (jana2000 in this example) must be defined in the environment variable *JANADIR*.

A.3.5 Memory requirements

After startup *Jana2000* uses about 40MB of memory (RAM). At the same time it reserves several hundreds MB of disk space for the virtual memory. The exact size depends on limits in params.cmn (see §A.2.5) but it is usually about 300MB. The amount of disk space does not depend on the size of RAM.

The RAM memory 64MB or larger is sufficient for running *JANA2000*. Larger memory speeds up the program as it minimizes usage of disk that is much slower than memory. Sometimes startup of *Jana2000* fails with message *"There is not enough free memory to run this program"*. This almost never means lack of RAM but rather insufficient disk space for virtual memory or unsuitable virtual memory limits.

Under Windows, the maximal and minimal size of the virtual memory can be limited by user with help of Control panel. The example below is for WindowsXP.



A.4 Results of testing refinements

Four testing examples are available in directory **test** for refinement of various structure types. The R-values should be close to the ones listed here.

Test A

Modulated structure with harmonic modulation of position and ADP

```
Overall R factors : [2723=2723+0/182]
S(obs) =  1.62 S(all)  =  1.62
R(obs) =  5.48 Rw(obs) =  7.19 R(all) =  5.48 Rw(all) =  7.19
R factors for main reflections : [728=728+0]
R(obs) =  4.33 Rw(obs) =  5.95 R(all) =  4.33 Rw(all) =  5.95
R factors for satellites of order 1 : [1373=1373+0]
R(obs) =  5.35 Rw(obs) =  6.69 R(all) =  5.35 Rw(all) =  6.69
R factors for satellites of order 2 : [622=622+0]
R(obs) = 11.37 Rw(obs) = 12.41 R(all) = 11.37 Rw(all) = 12.41
Maximum change/e.s.d. :   -0.0241 for B22cos1[As]
```

Test B

Modulated structure with harmonic modulation of occupation, position and ADP

```
Overall R factors : [1491=1324+167/129]
S(obs) =  1.36 S(all)  =  1.29
R(obs) =  3.75 Rw(obs) =  4.57 R(all) =  4.03 Rw(all) =  4.60
R factors for main reflections : [858=822+36]
R(obs) =  3.32 Rw(obs) =  4.09 R(all) =  3.44 Rw(all) =  4.10
R factors for satellites of order 1 : [633=502+131]
R(obs) =  6.45 Rw(obs) =  7.84 R(all) =  7.30 Rw(all) =  7.95
Maximum change/e.s.d. :    0.0221 for B11[P]
```

Test C

Standard structure with anharmonic ADP

```
Overall R factors : [412=412+0/45]
S(obs) =  1.21 S(all)  =  1.21
R(obs) =  3.07 Rw(obs) =  3.51 R(all) =  3.07 Rw(all) =  3.51
Maximum change/e.s.d. :    0.0011 for U12[Te1]
```

Test M

Test B with a rigid body

```
Overall R factors : [1491=1324+167/120]
S(obs) =  1.53 S(all)  =  1.44
R(obs) =  4.07 Rw(obs) =  5.14 R(all) =  4.37 Rw(all) =  5.17
R factors for main reflections : [858=822+36]
R(obs) =  3.47 Rw(obs) =  4.35 R(all) =  3.59 Rw(all) =  4.36
R factors for satellites of order 1 : [633=502+131]
R(obs) =  7.88 Rw(obs) =  9.96 R(all) =  8.74 Rw(all) = 10.08
Maximum change/e.s.d. :   -0.0275 for B12[P]
```

A.5 Troubleshooting

- ***The program cannot find some system files or it cannot read them properly.***

It is often because of wrong definition of *JANADIR*. It may point to some other version of *JANA*.

- ***The program cannot start due to lack of memory***

Very often, this is due to insufficient disk space or low limit for virtual memory size. See §A.3.5 for more information.

- ***Windows version cannot start or behaves unexpectedly***

The program is compiled for processors compatible with Intel Pentium Pro, Pentium II, III and IV. For older processors a special version can be obtained from the authors.

- ***Installation of UNIX version fails***

Try automatic installation instead of manual installation and vice versa. The instructions for manual installation are in §A.2.2 .

The cc, f77 or f90 compiler may not be installed or accessible. Try

```
which f77
whereis f77
find / -name f77 -print
```

Try to use f90 compiler instead of f77 and vice versa. This can be selected in the *Makefile*, see §A.2.2 .

The compiler cannot find *X11 include files* or *X11 library*. The information about the path to *X11 include files* is in the *Makefile* after the -I option (check the lines starting `INCLUDE = -I`. The information about the path to *X11 library* is written in the *Makefile* in the *LINKLIBS* macro (check the lines starting `LINKLIBS =` .

- ***The UNIX version does not work correctly after upgrading***

It may be problem with JANADIR – see above.
By upgrading we mean installation of a new version of the program to the same directory where the old version has been installed. The program *make* recognizes dependencies between files in order to compile only the necessary portion of the source code. Sometimes (very rarely) this fails and some of new source code is not compiled. The command

```
make CLEAN_up
```

deletes all compiled code so that *make* will compile the whole package. Another way is to compile the new version in a different directory[1]. This however requires to redefine *JANADIR* if it has been defined in shell startup scripts.

- ***The compiler for UNIX version has a bug***

Problems with compilers are reported in **Jana2000 homepage**[2], section *Known bugs*. Many of these problems are detected (and solved, if possible) by the automatic installation procedure in Jana2000Pack.exe.

g77, version 2.96 20000731 [1] distributed with Red Hat Linux contains a bug that influences the translation part of symmetry operators. Reading of the operators from

[1] *JANADIR* must be redefined accordingly.
[2] http://www-xray.fzu.cz/jana/jana.html

M50 works well but writing them back may destroy or change the translation parts. It happens with the testing example *Testa*. All versions of *g77* starting with 3. work correctly.

f90 in operating system IRIX 6.2 cannot compile *Jana2000*. It crashes during the compilation. *f77* in the same system works properly.

f77 in operating system IRIX 6.5 contains a bug that causes crash of *Jana2000* when using for instance the interface to the *Equation command* in the refinement commands. *f90* with the same system works properly.

f77 "Driver V5.2-10, Fortran 77 V5.2-171-428BH" in operating system OSF1[2] contains a bug that causes unexpected behavior of Jana2000 in many cases.

- ***The version for Windows cannot determine a proper font size. User preferences cannot be saved to jana2000.ini.***

During the first startup after installation, *Jana2000* for Windows makes a test to determine proper size of the system font that will be used for the graphical interface. After finishing the test the results are saved in jana2000.ini[3] that resides in the *JANADIR* directory. If the program repeats the test after next start or if the fonts are unreadable the test results probably could not be saved to jana2000.ini. This often happens for two reasons:
1. Jana2000.ini does not have the write permission. See §A.3.4 page 113 for more information.
2. The test fails because of the *Clear type* method used for smoothing edges of screen fonts under WindowsXP. The test relays on difference between dark text and white background that no longer exists with the *Clear type* method. Currently the only solution for *Jana2000* is to use *Standard* method or disable smoothing of screen fonts edges.

The part of jana2000.ini with information about screen fonts

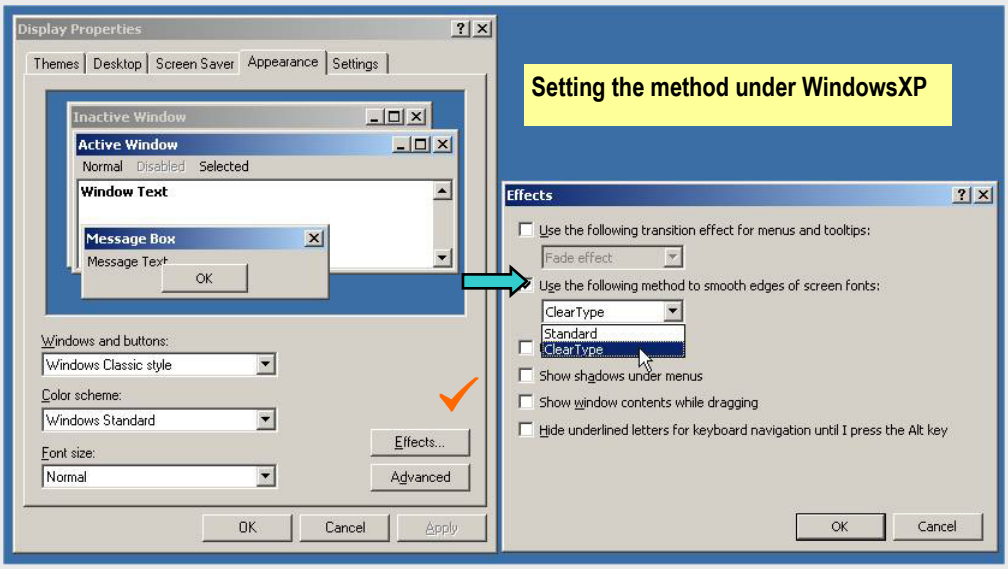
```
jana2000.BasicFontXScale: 0.85
jana2000.BasicFontYScale: 0.65
jana2000.BasicFontWidth: 3.143252
jana2000.BasicFontHeight: 4.542351
jana2000.BasicFontHeightCorr: 0.28429
```

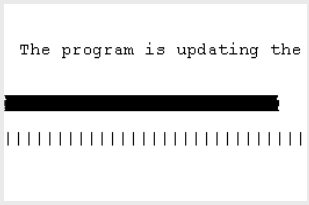
[1] The version information is printed by command `g77 -v`

[2] The version of f77 is printed by command `f77 -what`

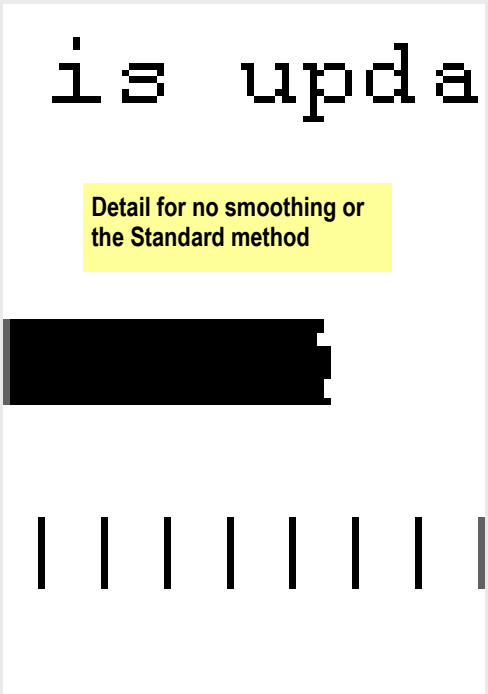
[3] The test is not done if the information is already present in jana2000.ini. We can force repeating of the test with Tools → Preferences → Check setting.

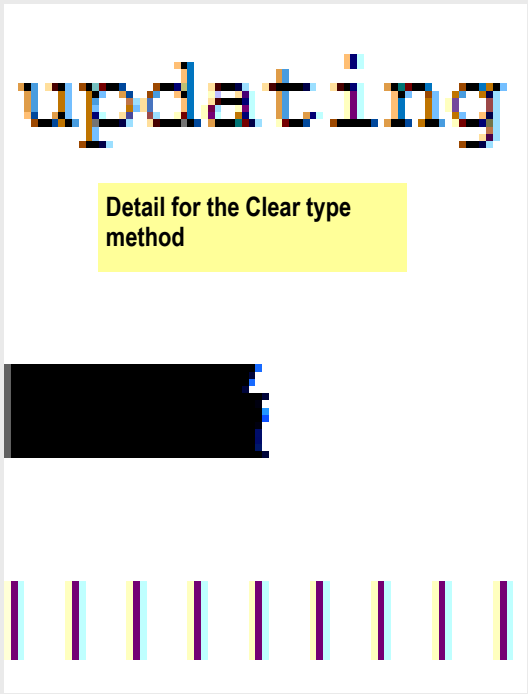
Smoothing screen font edges under WindowsXP





Font test in Jana2000





B User preferences

User preferences are set through *Tools* → *Preferences* and they are saved to jana2000.ini. For both versions, they can be used to set size and position of the *Jana2000* window, path to temporary space and external programs.

A.6 The configuration files jana2000.ini and jana2000.hst

Jana2000.ini contains the user preferences, for instance size of the window, fonts, path to external programs etc. All these settings can be defined through *Tools* →*Preferences*. Jana2000.hst contains list of the fifteen last structures and is used through *File* → *Structure* → *History* (see later in this Appendix).

Windows

In Windows version, the files are in the *JANADIR* directory. They must have write permission for users of *Jana2000* (see § A.3.4 page 113 for more information).

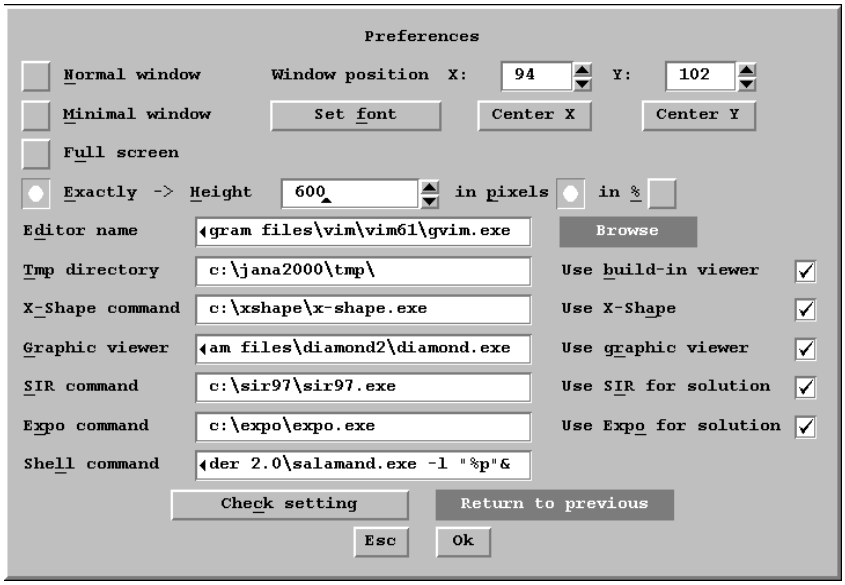
UNIX

In *UNIX* version, both files are in the user root directory. In order to support centralized installation of *Jana2000* in UNIX workstations jana2000.ini is interpreted in the following order:

- jana2000.ini in the directory *JANADIR*
- jana2000.ini in the user's root directory
- jana2000.ini in the working directory

The last read settings overwrite the precedent ones.

A.7 Preferences for Windows version



Most of the options are self-explanatory.

Browse starts File manager to find path to an external program. After quitting the File manager the found path is pasted to the active text box.

In the *Shell command*[1] *%p* stands for the name of the current directory and symbol *&* indicates *Jana2000* wills not wait for the finishing of the shell command.

[1] It is executed through File→Start shell.

Hardware fonts

Because of limitations of *Windows interacter* [13] *Jana2000* uses hardware fonts. They are not scalable and they exist only in several sizes. Moreover, information about their sizes is not reliable.

At the first startup, the program calculates a desired font size based on the window size. Then it selects the hardware font that is the closest one to the desired size. Then a special procedure measures the real size of the font and saves the results in jana2000.ini.

Set font can be used for changing the default hardware font by changing the desired size (in the user coordinates with approximately 1mm units). When we change the desired width or height the program looks for the closest hardware font and then repeats measuring of the real size. *Check setting* reruns measurement of the real size.

Two problems are often associated with this topic. Firstly, jana2000.ini must have write access for the user of *Jana2000*, see page 113. Secondly, some special font settings may disable the real size measurement – see Appendix A, Troubleshooting.

A.8 Preferences for UNIX version

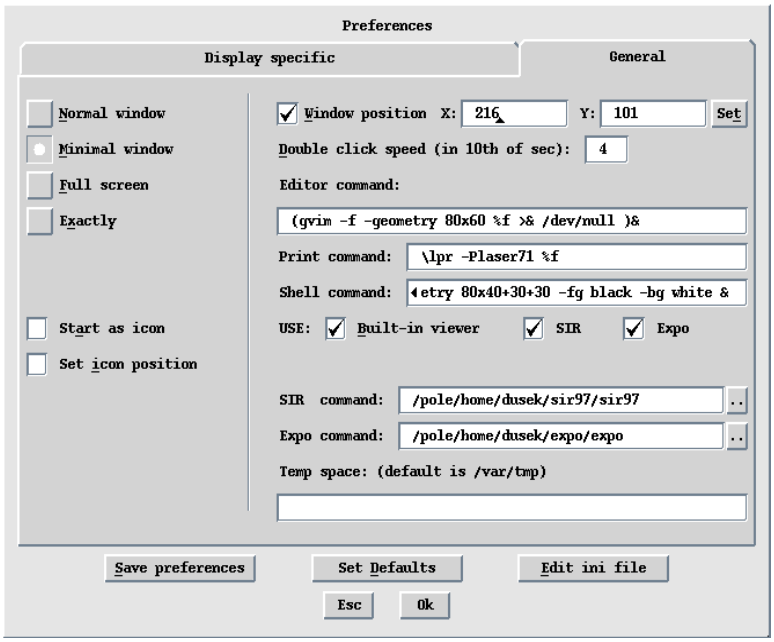
UNIX workstations are often used from more terminals that may differ by size, pixel resolution, available fonts etc. The terminal can be the workstation itself, some other UNIX workstation or a PC with Windows running emulation of X Windows[1]. In other words, the terminal is the computer that accepts and realizes graphical requests. It is usually called X-server and it has an address of form *IP_address:m.n*[2], for instance *pc222.fzu.cz:0.0*.

For UNIX version, we divide preferences to *General* and *Display specific*. The General preferences are valid for all terminals while the Display specific preferences are saved to jana2000.ini separately for every display address. Some preferences, for instance about the window size, are available in both General and Display specific part. The Display specific preferences override the General preferences so that the window size set in General preferences realizes only with display addresses that are not yet present in jana2000.ini. In addition, a hierarchy of *ini* files exists, see A.6 .

[1] X Windows is a window system based on X11 graphical library.

[2] *m* is number of the server, *n* is number of screen.

A.8.1 General preferences



Most of the options are self-explanatory.

The current window position is written to the *Window position* text boxes by the button *Set*. If the *x* coordinate is negative, it is understood as the distance between the right side of the window and the right side of the display. If the *y* coordinate is negative, it is understood as the distance between the bottom of the window and the bottom of the display. The same rule holds for *Icon position*.

The commands accept symbol *%d* for the default font of *Jana2000* and *%f* for file name. The symbol *&* has normal meaning, i.e. running on the background. *Jana2000* automatically removes *&* in cases where waiting for the result of the command is necessary.

Temporary space is implicitly the first directory from /scratch, /var/tmp, /tmp or *$(HOME*) detected by the program as accessible with write permission.

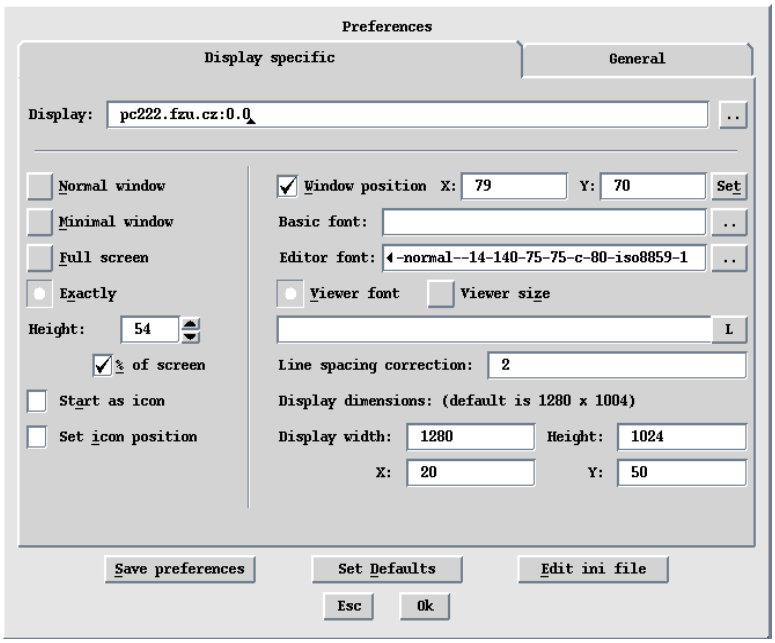
Examples of printer commands

lpr %f	Sends the output to the default printer.
lpr -Pname %f	Sends the output to the printer named name.
rcp %f remote.cz:work/pppp; rsh remote.cz "lpr -Pmyprinter work/pppp"	In this example, the file %f is copied to a remote computer that is then used for printing. The commands rcp and rsh can be replaced by more secure scp and ssh.
xterm -e prjana %f	The last command can be used when a dialogue precedes the printing. For instance, the print server may ask for login and password. The command opens the xterm window and immediately starts a procedure prjana with commands for connecting to the print server and printing.

Examples of editor commands

textedit -fn %d %f	This command opens file *%f* in *Textedit* using font *%d* (this is the font used by *Jana2000*).
emacs -font %d %f	Example of the editor command for *emacs* editor.
xterm -fn %d -e vi %f	This command starts *xterm* window and opens there file *%f* using editor *vi* and font *%d.* The *xterm* window is necessary as *vi* does not have its own window.
nedit %f	Example of the editor command for *nedit* editor.
gvim -f -geometry 80x60 %f	Example of the editor command for *gvim*. The key *-f* causes *gvim* do not run on the background, i.e. *Jana2000* waits for its exit.

A.8.2 Display specific preferences



Jana2000 recognizes automatically the display address and writes it to the *Display* textbox. With the button on the right of the textbox, we can switch to settings saved for some other display address. If we want to use for the current display the settings already saved for some other display address, we just switch to the settings and then retype the display name to the current display.

Secure shell changes display addresses

Secure shell changes display addresses. For instance the display address *pc222.fzu.cz:0.0* takes form *host.fzu.cz:m.0*, where *m* is usually greater then nine and *host* is the computer we are logged in. The number *m* is dynamically assigned by *ssh* so that the display address is no longer fixed. Moreover, the address of the display that we use as a terminal cannot be identified from the display address so that sorting of preferences by the display addresses loses the sense. Jana2000 does not solve this situation. Instead, we recommend changing of the *DISPLAY* variable from the secure form to the non-secure one before every start of *Jana2000*, for instance by command *(setenv DISPLAY yyyy:0; jana2000)&*. This solves not only the problem with display names for Preferences but at the first place is speeds up performance of the program as the X11 graphics is no longer encrypted. For more information, see Appendix A, page 110.

X11 fonts

At startup[1], *Jana2000* chooses automatically the *basic font* and the *viewer font*. If we use these default fonts, the relevant text boxes in *Preferences* are clear. The name of the basic font can be used in commands in *General Preferences* using the symbol *%d*.

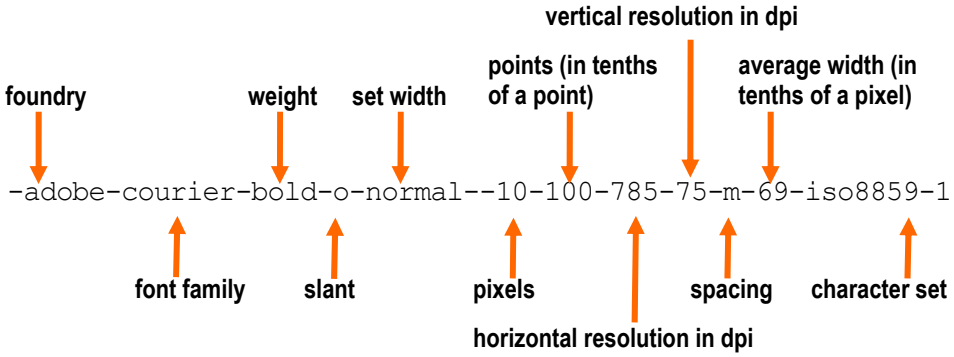
User fonts can be defined in *Preferences* through the *"."* buttons that display list of available monospaced fonts. The number of fonts in the list is usually large as they are not scalable. Some X Windows systems enable scaling of fonts but it is not supported in *Jana2000*. In Appendix C, there is more information about font names and scaling.

Line spacing correction is used for the built-in viewer to enlarge line spacing. t is entered in pixels.

Display dimensions are used for the definition of a virtual display for cases when an X server returns invalid information about display dimensions. The virtual display defines a visible area of the screen and the window position and size are defined with respect to this rectangle. If the display dimensions are changed, the position and window size are immediately recalculated in order to have the same window at the same place.

[1] The Windows version sets the fonts at the first startup. The UNIX version searches for the fonts at every startup. In both versions, the viewer font is set at the first startup of the listing viewer. Both versions repeat the searching if the size of Jana2000 window is changed.

C Font names in X Windows



foundry	The type foundry that digitized and supplied the font
set width	A value describing a font's proportionate width, according to the foundry.
pixels and points	Type is normally measured in points, a printer's unit equal to 1/72 of an inch. The size of a font in pixels depends on the resolution.
spacing	Either m (monospace, i.e., fixed-width) or p (proportional, i.e., variable-width)
horizontal and vertical resolution	The resolution in dots per inch for which a font is designed. Horizontal and vertical figures are required because a screen may have different capacities for horizontal and vertical resolution.
average width	Mean width of all characters in the font, measured in tenths of a pixel.
character set	ISO, the International Standards Organization, has defines character set standards for various languages. The iso8859-1 represents the ISO Latin-1 character set.

Scalable fonts have *average width*, *pixels* and *points* fields equal to zero. More information is available in Appendix A of [10].

D Formats of files used by Jana2000

In preparation

E Weighting scheme

In preparation

F Graphic libraries

In preparation

G Tables for publication

To facilitate creation of tables text files jobname.tb? are produced by *Tools → special tools → tables for publications*. In the files, the semicolon stands for columns delimiter and the caret symbols close the text that should be printed as a superscript. Here we present a macro for Microsoft Word that processes a rough table of distances saved in file naco1.tbd for structure of Na2CO3 discussed in the chapter 1.4 . The macro can be downloaded from WWW page of Jana2000 as **MkTableJana.zip**.[1]

The file of distances produced by Jana2000

```
Na1-O1a^i^;2.4346(12);2.4158(11);2.4461(12)
Na1-O1a^i^;2.4344(12);2.4158(11);2.4461(12)
Na1-O2a;2.3261(15);2.2890(16);2.3490(15)
Na1-O2a^i^;3.7032(14);3.4069(15);3.9672(15)
Na1-O2a^ii^;2.3264(15);2.2890(16);2.3490(15)
Na1-O2a^i^;3.7071(14);3.4068(15);3.9671(15)
Na1-O2a^iii^;2.3263(15);2.2890(16);2.3490(15)
Na1-O2a^iv^;3.7030(14);3.4068(15);3.9671(15)
Na1-O2a^v^;2.3264(15);2.2890(16);2.3490(15)
Na1-O2a^vi^;3.7066(14);3.4069(15);3.9672(15)
Na2-O1a;2.3404(14);2.3181(13);2.3564(13)
Na2-O1a^vii^;2.3404(14);2.3181(13);2.3564(13)
Na2-O2a^viii^;2.3768(14);2.3368(12);2.4326(15)
Na2-O2a^ix^;2.3768(14);2.3368(12);2.4326(15)
Na2-O2a^x^;2.3774(14);2.3368(12);2.4326(15)
Na2-O2a^xi^;2.3776(14);2.3368(12);2.4326(15)
Na3-O1a;2.6149(15);2.5682(15);2.6746(15)
Na3-O1a^xii^;2.6754(11);2.4544(11);2.9086(11)
Na3-O1a^ix^;2.6711(11);2.4544(11);2.9086(11)
Na3-O2a;3.6054(19);3.331(2);3.8576(19)
Na3-O2a^vii^;2.9585(18);2.6460(18);3.2425(17)
Na3-O2a^xiii^;2.6325(16);2.4022(16);2.9122(15)
Na3-O2a^ix^;2.6006(15);2.4092(15);2.8386(15)
Na3-O2a^xiv^;2.6345(16);2.4022(16);2.9122(15)
Na3-O2a^x^;2.5966(15);2.4092(15);2.8386(15)
Na3-O2a^iv^;3.6067(19);3.331(2);3.8576(19)
Na3-O2a^xv^;2.9641(18);2.6460(18);3.2425(17)
C1a-O1a;1.2830(15);1.2762(14);1.2915(15)
C1a-O2a;1.2807(12);1.2617(13);1.2922(12)
C1a-O2a^xiii^;3.7814(16);3.3902(16);4.1729(16)
C1a-O2a^i^;3.5258(16);3.1920(16);3.8353(15)
C1a-O2a^xiv^;3.7822(16);3.3902(16);4.1729(16)
C1a-O2a^xvi^;3.5254(16);3.1920(16);3.8353(15)
C1a-O2a^iv^;1.2807(12);1.2617(13);1.2922(12)

(i)                 1/2-x,1/2-y,-z
(ii)                1-x,1-y,-z
(iii)               1+x,-y,z
(iv)                1/2+x,1/2-y,z
(v)                 1/2+x,3/2-y,z
(vi)                x,-y,z
(vii)               -x,-y,1-z
(viii)              -1/2-x,-1/2-y,-z
(ix)                1/2-x,1/2-y,1-z
(x)                 1/2+x,-1/2-y,1+z
(xi)                -1+x,-y,z
(xii)               1/2-x,-1/2-y,1-z
(xiii)              1-x,-y,1-z
(xiv)               1+x,-y,1+z
(xv)                1/2+x,1/2-y,1+z
(xvi)               1/2+x,-1/2-y,z
```

[1] http://www-xray.fzu.cz/jana/Jana2000/manual/examples/MkTableJana.zip

The Microsoft Visual Basic macro for Word

```
Sub MkTableJana()

'
' MkTableJana Macro
'
    If Selection.Words.count <= 1 Then
      MsgBox ("The table must be selected by mouse " + Chr$(13) + _
             "before the macro is started")
      GoTo konec
    End If

' The table is created from selected text, ";" is delimiter
    Selection.ConvertToTable Separator:=";", _
        NumColumns:=4, NumRows:=5, AutoFitBehavior:=wdAutoFitContent

' The text closed between "^" is changed to superscript
' The caret symbols are then deleted
    Selection.Find.ClearFormatting
    Selection.Find.Replacement.ClearFormatting
    With Selection.Find
        .Text = "^^*^^"
        .Replacement.Text = ""
        .Forward = True
        .Wrap = wdFindStop
        .Format = True
        .Replacement.Font.Superscript = True
        .MatchCase = False
        .MatchWholeWord = False
        .MatchAllWordForms = False
        .MatchSoundsLike = False
        .MatchWildcards = True
    End With
    Selection.Find.Execute Replace:=wdReplaceAll
    Selection.Find.ClearFormatting
    Selection.Find.Replacement.ClearFormatting
    With Selection.Find
        .Text = "^"
        .Replacement.Text = ""
        .Forward = True
        .Wrap = wdFindStop
        .Format = True
        .MatchCase = False
        .MatchWholeWord = False
        .MatchWildcards = False
        .MatchSoundsLike = False
        .MatchAllWordForms = False
    End With

' The legend lines are merged, separated by ";".
' Spaces are deleted
    Selection.Find.Execute Replace:=wdReplaceAll
    Selection.Find.ClearFormatting
    With Selection.Find
        .Text = "(i)"
        .Forward = True
        .Wrap = wdFindStop
        .Format = True
        .MatchCase = False
        .MatchWholeWord = False
        .MatchWildcards = False
        .MatchSoundsLike = False
        .MatchAllWordForms = False
    End With
    Selection.Find.Execute
    If Selection.Find.Found = True Then
      Selection.MoveEnd unit:=wdTable
      Selection.Cells.Merge
```

```
      Selection.Rows.HeightRule = wdRowHeightAuto
      Selection.Find.ClearFormatting
      Selection.Find.Replacement.ClearFormatting
      With Selection.Find
          .Text = "^p"
          .Replacement.Text = "; "
          .Forward = True
          .Wrap = wdFindStop
          .Format = False
          .MatchCase = False
          .MatchWholeWord = False
          .MatchWildcards = False
          .MatchSoundsLike = False
          .MatchAllWordForms = False
      End With
      Selection.Find.Execute Replace:=wdReplaceAll
      Selection.Find.ClearFormatting
      Selection.Find.Replacement.ClearFormatting
      With Selection.Find
          .Text = "  "
          .Replacement.Text = " "
          .Forward = True
          .Wrap = wdFindStop
          .Format = False
          .MatchCase = False
          .MatchWholeWord = False
          .MatchWildcards = False
          .MatchSoundsLike = False
          .MatchAllWordForms = False
      End With
      While Selection.Find.Found = True
        Selection.SelectCell
        Selection.Find.Execute Replace:=wdReplaceAll
      Wend
    End If
konec:
End Sub
```

The resulting table in Word

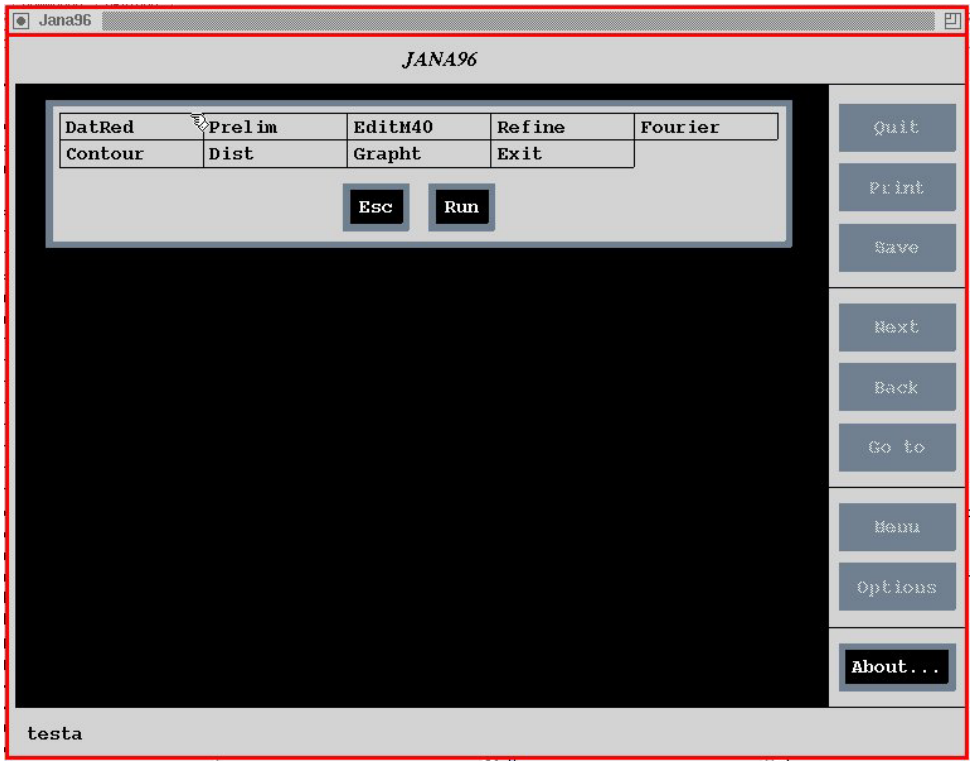
Na1-O1a^{i}	2.4346(12)	2.4158(11)	2.4461(12)
Na1-O1a^{i}	2.4344(12)	2.4158(11)	2.4461(12)
Na1-O2a	2.3261(15)	2.2890(16)	2.3490(15)
Na1-O2a^{i}	3.7032(14)	3.4069(15)	3.9672(15)
Na1-O2a^{ii}	2.3264(15)	2.2890(16)	2.3490(15)
Na1-O2a^{i}	3.7071(14)	3.4068(15)	3.9671(15)
Na1-O2a^{iii}	2.3263(15)	2.2890(16)	2.3490(15)
Na1-O2a^{iv}	3.7030(14)	3.4068(15)	3.9671(15)
Na1-O2a^{v}	2.3264(15)	2.2890(16)	2.3490(15)
Na1-O2a^{vi}	3.7066(14)	3.4069(15)	3.9672(15)
Na2-O1a	2.3404(14)	2.3181(13)	2.3564(13)
Na2-O1a^{vii}	2.3404(14)	2.3181(13)	2.3564(13)
Na2-O2a^{viii}	2.3768(14)	2.3368(12)	2.4326(15)
Na2-O2a^{ix}	2.3768(14)	2.3368(12)	2.4326(15)
Na2-O2a^{x}	2.3774(14)	2.3368(12)	2.4326(15)
Na2-O2a^{xi}	2.3776(14)	2.3368(12)	2.4326(15)
Na3-O1a	2.6149(15)	2.5682(15)	2.6746(15)
Na3-O1a^{xii}	2.6754(11)	2.4544(11)	2.9086(11)
Na3-O1a^{ix}	2.6711(11)	2.4544(11)	2.9086(11)
Na3-O2a	3.6054(19)	3.331(2)	3.8576(19)
Na3-O2a^{vii}	2.9585(18)	2.6460(18)	3.2425(17)
Na3-O2a^{xiii}	2.6325(16)	2.4022(16)	2.9122(15)
Na3-O2a^{ix}	2.6006(15)	2.4092(15)	2.8386(15)
Na3-O2a^{xiv}	2.6345(16)	2.4022(16)	2.9122(15)
Na3-O2a^{x}	2.5966(15)	2.4092(15)	2.8386(15)
Na3-O2a^{iv}	3.6067(19)	3.331(2)	3.8576(19)
Na3-O2a^{xv}	2.9641(18)	2.6460(18)	3.2425(17)
C1a-O1a	1.2830(15)	1.2762(14)	1.2915(15)
C1a-O2a	1.2807(12)	1.2617(13)	1.2922(12)
C1a-O2a^{xiii}	3.7814(16)	3.3902(16)	4.1729(16)
C1a-O2a^{i}	3.5258(16)	3.1920(16)	3.8353(15)
C1a-O2a^{xiv}	3.7822(16)	3.3902(16)	4.1729(16)
C1a-O2a^{xvi}	3.5254(16)	3.1920(16)	3.8353(15)
C1a-O2a^{iv}	1.2807(12)	1.2617(13)	1.2922(12)

(i) 1/2-x,1/2-y,-z; (ii) 1-x,1-y,-z; (iii) 1+x,-y,z; (iv) 1/2+x,1/2-y,z; (v) 1/2+x,3/2-y,z; (vi) x,-y,z; (vii) -x,-y,1-z; (viii) -1/2-x,-1/2-y,-z; (ix) 1/2-x,1/2-y,1-z; (x) 1/2+x,-1/2-y,1+z; (xi) -1+x,-y,z; (xii) 1/2-x,-1/2-y,1-z; (xiii) 1-x,-y,1-z; (xiv) 1+x,-y,1+z; (xv) 1/2+x,1/2-y,1+z; (xvi) 1/2+x,-1/2-y,z

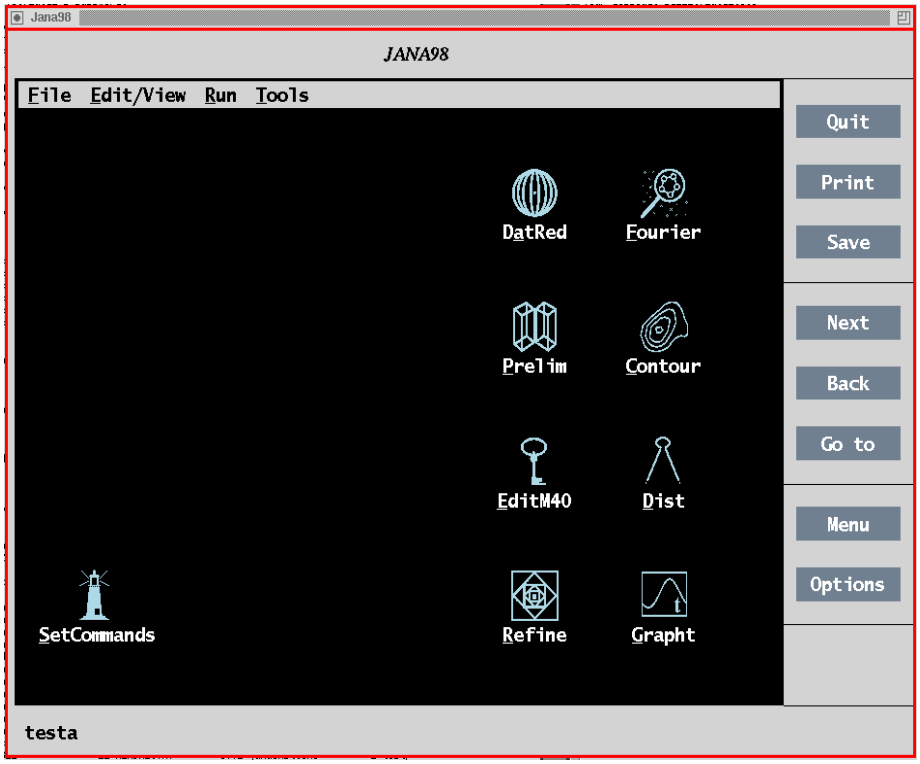
H History

The first version of the refinement program *Jana* was written in 1984 by Václav Petříček during his stay in the group of Prof. Coppens in Buffalo, USA. The program system *Jana94* consisted of refinement program, program for Fourier synthesis and some interpretation programs. Its parts were executed as separate programs in the traditional alphanumeric mode.

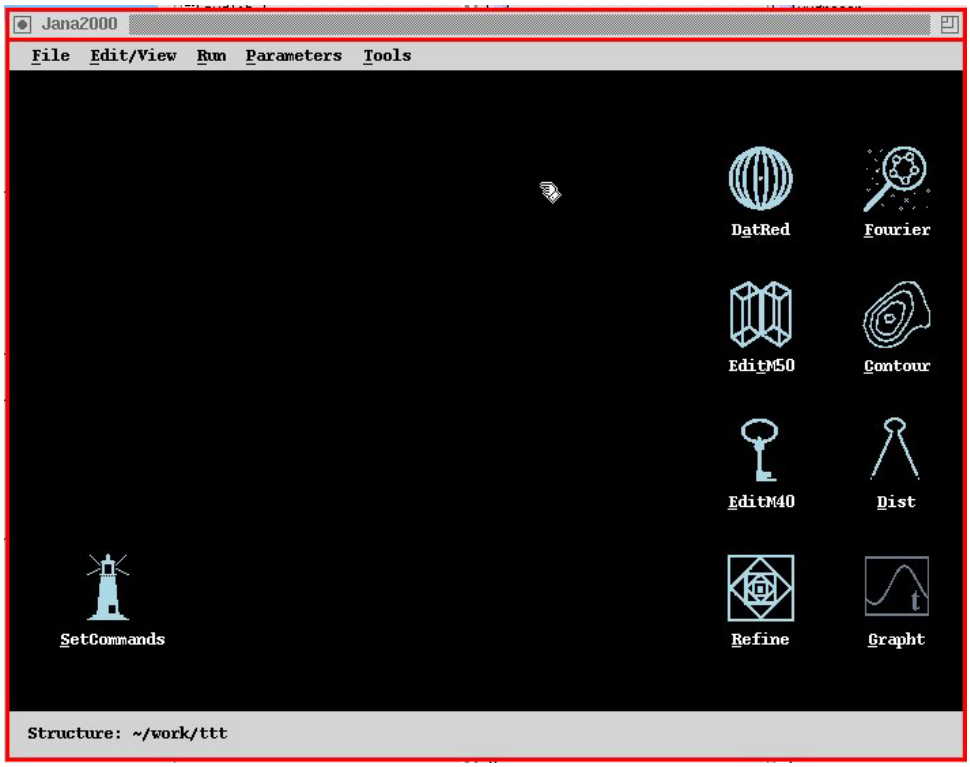
With development of computer equipment, we were able to join these programs to a single body with simple graphical interface and we called this system *Jana96*. This version was used by almost 100 users around the world. The UNIX version of *Jana96* was already based on X11 graphics library but the PC version was a DOS program.



Further development of computers, especially larger operating memory, enabled combination of methods used for three-dimensional structures and modulated structures into a single program *Jana98*. From this year, we say we are developing a unified system for crystallographic computing with particular attention to user-friendly interface and uniform access to 3- and more-dimensional crystals. *Jana98* has been used by almost 250 users. The PC version of *Jana98* was still a program for DOS.



The current version of the program is called *Jana2000*. The PC version is now 32 bits program using Windows API graphics. *Jana2000* integrates work with standard and modulated structures calculated from single crystal or powder data. It also includes multipole refinement. *Jana2000* is used by almost 600 of registered users.



Contents (detailed)