REFSPC_01
MANUAL

GENERAL

The program REFSPC calculates and fits the Mössbauer spectra of reflectivity for specified grazing angles, the angular dependencies of the X-rays and nuclear resonance reflectivity and CEMS spectra measured at normal incidence from any multilayer structure containing Mössbauer isotope ^{57}Fe. The calculations of reflectivity are performed for the p-polarized radiation – that is the polarization of radiation from Synchrotron Mössbauer Source (Potapkin V., Chumakov A. I., Smirnov G. V., Celse J.-P., Rüffer R., McCammon C., Dubrovinsky L., J. Synchrotron Rad. **19,** 559 (2012).). You can calculate just theoretical dependencies or upload the experimental data and fit them. The results immediately appear on the screen. Besides, in the additional windows you can also view the depth distribution of the electronic density and nuclear density for different kinds of the hyperfine fields in the model which you have chosen.

OPERATIONS

The pack "**REFSPC.ZIP**" contains the main "**REFSPC.exe**" (which opens the main window) and the set of the executable files:

"**SpecRef.exe**" and "**SpecR_Am.exe**" - for calculations and fit of the Mössbauer spectra of reflectivity;
"**RefNucl.exe**" and "**RefN_Am.exe**" - for calculations and fit of the nuclear (including X-ray) reflectivity;
"**RefXray.exe**", "**RefX_Am.exe**" and "**RefX_NET.exe**" for calculations and fit of the X-ray reflectivity;
"**CEMS_S.exe**" and "**CEMS_Am.exe**" for calculations and fit of the CEMS spectra.

Comment:
The executable files for calculations are specified now in the external file ("**EXEC.INP**") so the presented graphic interface can be used for any other kind of calculations (e.g. in order to calculate the spectra of the forward scattering, in order to include the existence of the additional resonant absorber before the reflection from an investigated sample, in order to install a new type of the fitting procedure. Remember that in this substitution you should keep the names of the output files for graph presentation.

The calculations need the input files.
The obligatory file "**Tconst.INI**" (contain the basic Mössbauer parameters of the nuclear transition – now it is prepared for 14.4 keV ^{57}Fe) is attached.

Calculations for another Mössbauer isotopes are possible. In this case the file "**Tconst.INI**" should be reloaded by **"Settings"** → "**Select isotope**" from the menu-line. The files "**FeConst.INI**, "**EuConst.INI**", "**SnConst.INI**", "**SmConst.INI**" are prepared for 4 Mössbauer transitions: 14.4 keV in ^{57}Fe, 21.532 keV in ^{151}Eu, 23.871 keV in ^{119}Sn and 22.494 keV in ^{149}Sm and they exist in the previous version REFTIM 7_4 pack. However, at the moment the nuclear monochromator for the measurements of the energy resolved Mössbauer spectra of reflectivity is created just for 14.4 keV

Mössbauer transition in ^{57}Fe. Some limitations of the present calculations take place: the noncollinear hyperfine interactions are considered only for the transition ½ → 3/2.

The other needed input files are created automatically

Exec.inp   Fil_exp.inp   Filem.inp   Calcul.inp   Refangl.inp   Fil_cems.inp   Axisf.inp   Next.inp   Stop.inp

when in the main REFSPC window (which is opened by "**REFSPC.exe**") you press the buttons "**Settings**" → "**Start from zero**":
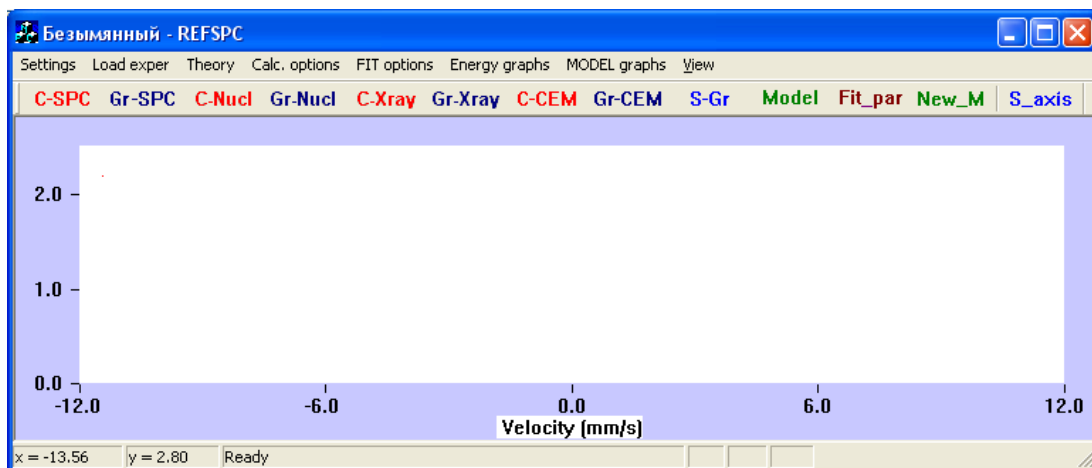

Fig. 1

They are:

"**EXEC.INP**" determines the choice of the executable and input files, it is corrected by "**Settings**" → "**Executable files**";

"**FIL_exp.INP**" gives the number and the names of the experimental Mössbauer spectra of reflectivity (if the are); it is fulfilled by "**Load experiment**" button − this dialog window determines all kind of the experimental data which you have for the sample and which you will use for fit using one and the same model file;

"**FILEM.INP**" gives the name of the model file and the angles at which the Mössbauer spectra of reflectivity will be calculated (max. number of spectra is 4); it is corrected in dialog by "**Theory**" → "**Model file**";

"**Calcul.INP**" characterizes the options for the reflectivity spectrum calculations; it is corrected by "**Calc. options**" → "**Energy spectra**" (file or dialog); this file can be renamed with corresponding changing in "**EXEC.INP**";

"**Refl.INP**" determines the input parameters for calculations and fit of the experimental angular x-ray and nuclear resonance reflectivity curves; it is corrected by "**Calc. options**" → "**X-ray and Nuclear refl**"; this file can be renamed with corresponding changing in "**EXEC.INP**";

"**CEMS.INP**" determines the input of the experimental CEM spectra and parameters of its calibration, theoretical calculations and fit; it is corrected by "**Calc. options**" → "**CEMS options**"; this file can be renamed with corresponding changing in "**EXEC.INP**";

"**AXISF.INP**" is the file where the scales of different graphs is determined (they can be changed by pressing the right button of mouse on the each graph and next by pressing "**S-axis**");

"**NEXT.INP**" is the file where the sequence of the fitted parameters is determined (the choice is described in the section "**VARIATIONS of the MODEL PARAMETERS**"; on default no parameters are chosen, you can watch it by "Fit_par";

"**STOP.INP**" is the special file for finishing the procedure of fitting at any moment with saving the last result, just you should write in this file "0", instead of normally existing "1". It is opened by "**FIT options**" → "**Stop calculations**".

If you have and load the experimental Mössbauer spectra of reflectivity they immediately appear in the initial window (if the format of the data file with experimental dependencies is correct – the examples is done ("M027.dat", "M029.dat") in the separate directory "**EXAMPLE**" in which you can start the program by "**REFSPC**" → "**Settings**" → "**Get previous settings**"). The other experimental data should appear (if you have loaded them) by pressing "Gr-Nucl", or "Gr-Xray", or "Gr-CEM". "Gr-SPC" returns you to the Mössbauer spectra of reflectivity.

The most essential thing for calculation is the right model file which will be used for all kinds of calculations. When you press "**Start from zero**" the program suggests you to create the right model file by sequent description of the Mössbauer parameters and layer characterization. It you will just press "OK" for all suggestions, the simplest model file will be created ("m.inf"), which will include just substrate and 1 Mössbauer sextet 33 T and B_{hf} oriented perpendicular to the surface.

You can look at the content of this file by button "**Model**", or "**Theory**" → "**corrections**". You can change any parameter in this file and if you'll save the changes, the calculations will be done with these new set of the parameters. Practically it is more convenient to save the corrected file with new name and to point out in the opening dialog that the following calculations will be preformed with the new model file.

If you have no any experimental file you can have just theoretical spectra and angular curves by buttons: "C-SPC", "C-Nucl", "C-Xray" and "C-CEM" respectively. The program remembers the first calculations and in the following calculations with new model file the previous result appears by dash lines. If the new calculations you want to be saved before the next calculations you can press "S-Gr".

In the additional windows you can also view the depth distribution of the electronic density and photoabsorption (normalized to that ones in α-Fe) by "**Model graphs**" → "**El density"** and depth distribution of the nuclear density for each multiplet by "**Model graphs**" → "**HFI graph**".

The Mössbauer spectra of absorption for two polarizations of the incident beam (at grazing angle) is presented by buttons "**Energy spectra**" → "**Absorption**", and Mössbauer spectra of reflectivity at the angles determined for calculations by the buttons "**Energy spectra**" → "**Reflectivity**".

MODEL DESCRIPTION

Here we describe the model parameters which the program has as the input for all calculations. The model file can be created through the dialog, which is opened by the buttons "**Theory**" → "**Create MODEL**" (or when you press "**Settings**" → "**Start from zero**").

First of all you should print in the dialog box the name of the model file, which you are creating (in default it is "**m.inf**"). Then you should point out the amount of the layers NNN characterizing the model structure, the numbers of the starting and final layer which are repeated in the structure N1N and N2N and the number of repetitions NRN. In default they are 1, 1, 1, 1, i.e. we consider just semi-infinite medium (substrate), no repetitions of layers. The maximum amount of layers in consideration NNN (without repetition and interface steps) is N24=8**0**. After automatic sub-division of the interfaces into several steps this maximum number could be 3**00**. The number of repetitions NRN of chosen sequence of sublayers from N1N up to N2N is arbitrary.

In the same dialog window you should print the number of different types of hyperfine fields (multiplets), which you will use for the calculation of the theoretical spectra of reflectivity NM (the maximum number of NM is N6=8 in this version). In default it is 1. If you have more than 1 multiplet you should print the expected ratio of the partial resonant spectra weights (areas) S(K), K=1,..NM. In default S(1)=1.00, and others are 0. They can be taken from the fit of the measured CEMS spectrum (if you have it).

Than you should determine if the hyperfine field orientation will be attributed to the definite layer (IBHF=1) or to the definite multiplet (IBHF=2).

Different types of normalization of the matrix of the nuclear density V in the structure is supposed. They are the parameters INORM and ISQ. If INORM=1 then the maximal value of the nuclear density is fixed and determined by the parameter HKMAX. HKMAX is 1.00 for pure α-iron with 95% enrichment and if the Mössbauer effect probability is 0.7. For INORM=2 the normalization of the nuclear density to HKMAX is applied only if the total density in some layer is larger than HKMAX. If INORM=3 then no normalization is applied. If INORM=4 then the normalization to HKMAX is applied only for a selected layer where the total density is larger than HKMAX. The parameter ISQ also determine the way of the nuclear density normalization: if you keep the relative amount of nuclei with each kind of hyperfine interaction S(K) (e.g. according to the fit of the CEM spectrum) then you put ISQ=0. If this relative amount is varied freely during the fit then we should put ISQ=1, in this case the resultant S(K) are changed during the fit. We can also keep the relative amount of resonant nuclei with definite HFI in each layer, then ISQ=2.

When you press "OK" you get the next dialog sheets in which you should characterize each multiplet (separate sheet for each multiplet).

Each multiplet is characterized by the value of magnetic hyperfine field ($B_{hf}(K)$), width of B_{hf} distribution ($dB_{hf}(K)$), isomer shift (IS(K)), electric field gradient (EFG(K)), additional line width (GRd(K)). Then you point out the angular parameters of B_{hf} orientation which are essential only if you have already choose IBHF=2. They are the polar BE(K) and azimuth GA(K) angels for B_{hf} orientation relative to the surface normal and to the normal to the scattering plane (i.e. BE=90° and GA=90° means that the magnetic hyperfine field is oriented along the beam), relative amount of nuclei with random in space orientation or random in the surface plane orientation of B_{hf} (parameters RAND(K) and PLAN(K), the sum of them can not be greater than 1). The last box in the dialog sheet is the angular distribution of B_{hf} orientations (parameter WID(K)). If IBHF=1 the same angular parameters refer to the definite sublayer and should be pointed out in the description of each sublayer (in the model file these parameters for the case IBHF=1 will be placed in the lines characterizing HFI in each sublayer).

Important note

As opposed to the previous version of the program pack "REFTIM", it is now possible to consider asymmetric electric field gradient and noncollinear B_{hf} and main axis of the electric field gradient. Corresponding values of the angles and parameter of asymmetry for

each multiplet should be inserted in the final file by hand (by button "Model", or "Theory" → "corrections", but not by dialog). Ab initio the asymmetry is supposed to be absent and the corresponding angular and asymmetry parameters are presented as 0 in the bottom lines of the constructed model file. This option is working only for the ½ → 3/2 nuclear transitions and for its usage you should choose IBHF=2.

Then the separate dialog sheets appear consequently for each layer j which you should fill. Each layer is characterized by the thickness H1A(j) (in Angstroms, for the substrate it is unessential) and by the electronic density and photoabsorption in each layer EL.DENS(j), actually they are the real and imaginary parts of the susceptibility (in 10^{-6} dimensionless units). The interface profiles are used for the description of the density variations (i.e. roughness) and HFI distributions in interfaces. The interfaces are characterized by the width of the upper interface of each layer j – WIDTH(j) - for each layer, by the number of steps KSTEP(j) for the interface function approximation in the reflectivity calculations. The different types of the interface functions KIND1(j), KIND2(j) are used for the real and imaginary parts of the electronic susceptibility and the nuclear density of each kind of HFI KINDV(j,K) (K=1,…N6, j=1,…NNN). You should also determine the parameters of the used functions ZD1(j), ZD2(j), ZDV(j,K), (K=1,…N6, j=1,…NNN) respectively for each interface (if they are needed for chosen type of functions).
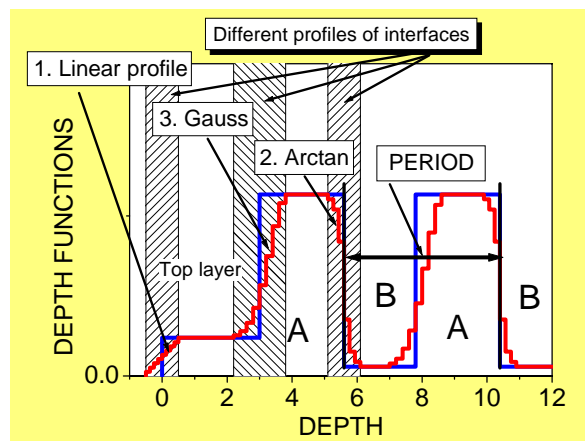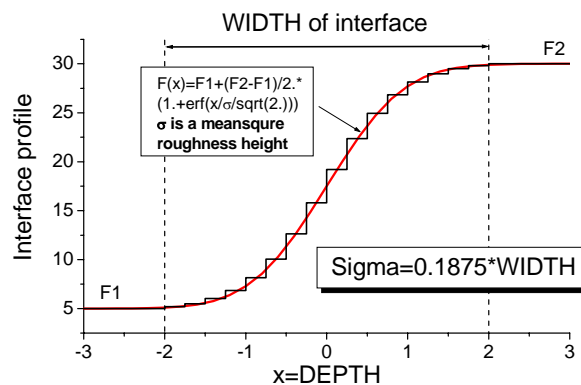

Fig. 2.

Fig. 3

The following kinds of the interface functions (KIND1, KIND2 or KINDV) are possible to choose: 1 − linear function (no additional parameters), 2 − arctangent, 3 − half Gauss

profile, 4 –Gauss profile, 5 – error function (no additional parameters). The characteristic shape of the interface functions 2, 3 and 4 (e.g. the width of Gauss function or the steepness of arctangent) are determined by additional parameters ZD1, ZD2, ZDV respectively. The different available functions are illustrated by Figs. 2,3.

The steepness of the error function is fixed. In this case the interface WIDTH is connected to the meansquare roughness height σ (which is often used in the reflectivity calculation as the suppression factor of Fresnel reflectivity at each boundary $e^{-2k^2\sigma^2}$) by the relation σ= 0.1875*WIDTH. (this factor was adjusted empirically).

Nuclei with each type of HFI can be distributed in the multilayer structure by their own manner. The depth distribution function is determined by the matrix V[j,K] which is actually the density of nuclei (normalized to the density of Fe atoms in pure α-Fe) with the definite type K of HFI in the layer with number j. During the calculations the depth profiles of V[j,K] will include the pre-described steps at the interfaces.

In the dialog "**Theory**" → "**Create MODEL**" we should fill the values of V[j,K] for K=1, .. NM in each j=1, …, NNN layer (NNN is determined on the first sheet), accordingly to the appearing sheets. For the description of the HFI distributions in the interfaces the same width and number of steps is used as it has been chosen for the electronic susceptibility description (parameters WIDTH and KSTEP). However the kind of function in each interface can be chosen independently. That is a matrix of integer numbers KINDV(j,K) (K=1,…N6, j=1,…NNN) for each type of HFI and each interface. The meaning of these numbers 1, 2, 3, 4 and 5 is the same as for the description of the susceptibility interface functions. Accordingly the matrix ZDV(j,K), (K=1,…N6, j=1,…NNN) should be filled, the elements of which describe the parameter of the interface functions (for 2,3,4 types of functions) for each kind of multiplet in each layer. In the same layer sheets you put the values of the angular parameters for each layer (BE, GA, RAND, PLAN, WID) if in the first sheet you have chosen the special parameter IBHF=1.

If you are going to investigate just the behavior of the theoretical spectra, then it is not necessary to have experimental data file (but you should create the model file). For this option the number of experimental spectra in consideration should be pointed out as 0.

If you would like to change the model essentially (e.g. to change the number of the layers NNN or the number of multiplets NM for the description of the spectra), it is recommended to go again to the dialog "**Theory**" → "**Create MODEL**", and from the begining change the numbers NNN and NM. In such a way you will be sure that the new model file will have the right format for calculations. By handle change of the model file you should be careful about the number of lines in the description of the sublayer thicknesses, HFI depth distribution description, kind of interface function for each multiplet in each layer and parameters of interface function for each multiplet in each layer.

THE EXPERIMENTAL DATA FILES

You can simultaneously view and fit up to 4 experimental Mössbauer spectra of reflectivity measured at different angles. The experimental data file should contain two columns of real numbers in text format. The first column is velocity in mm/s (the argument sequence should be ascending ! – take care of the data from ID18 because this sequence is

opposite) and the second column is the intensity of reflectivity. The total number of lines should not be larger than 900.

The examples of the reflectivity spectrum data files are given in the "**EXAMPLE**" directory, they are "M027.dat" and "M029.dat". In the main window they looks in the following way:
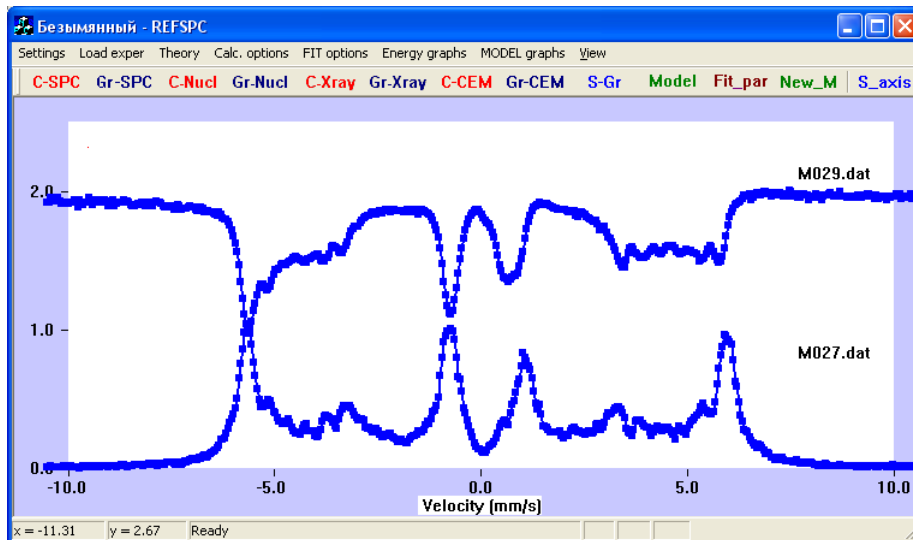

Fig. 4.

The x-ray and nuclear resonance reflectivity experimental data files in the first line present the number of angular points at which the reflectivity has been measured (max number of points for X-ray reflectivity dependencies is 3500, for the nuclear reflectivity – 900) and from the second line we should have two columns. The first column is the grazing angle in mrad, the second column is the intensity of reflectivity: for x-ray or nuclear reflectivity you should have separate files.

The examples of the reflectivity angular curves are given in "**EXAMPLE**" directory, they are "A3Xref84.DAT" and "A3Nref84.DAT" for x-ray or nuclear reflectivity respectively. When you load these files (or use the previous settings in "**EXAMPLE**") and press "Gr-Nucl" you will see this window. The data on the graph are normalized, but the nuclear reflectivity is multiplied for 0.01 for better view.
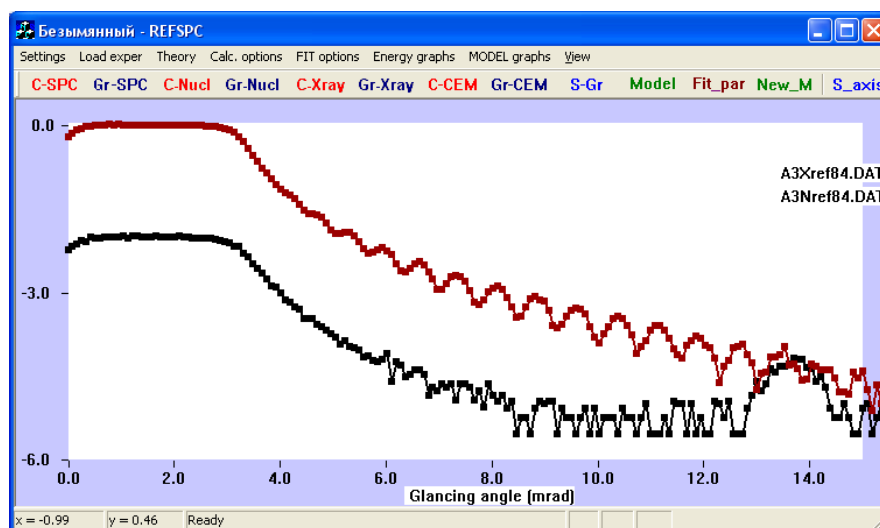

Fig. 5.

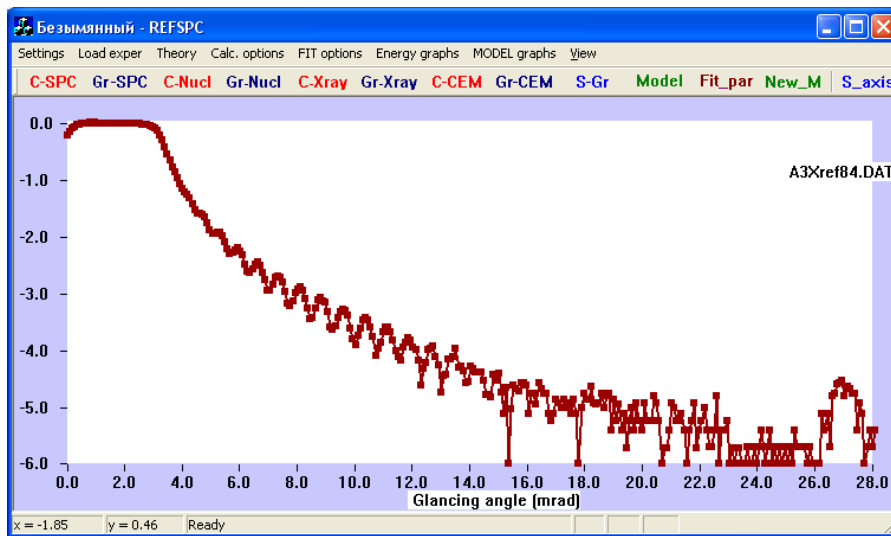If you press "Gr-Xray" you will see this window:

Fig. 6.

The experimental CEMS spectrum should be given as single column counts data and in order to have the spectrum on the screen (and for its fit) you should have the calibration data, which should be inserted into the "**CEMS.INP**". The example of the CEMS data file is given in "**EXAMPLE**" directory, it is "**MA14_5.dat**". The calibration data for this file are given in the presented "**CEMS_A3.INP**". If you press "Gr-CEM" you will see this window:
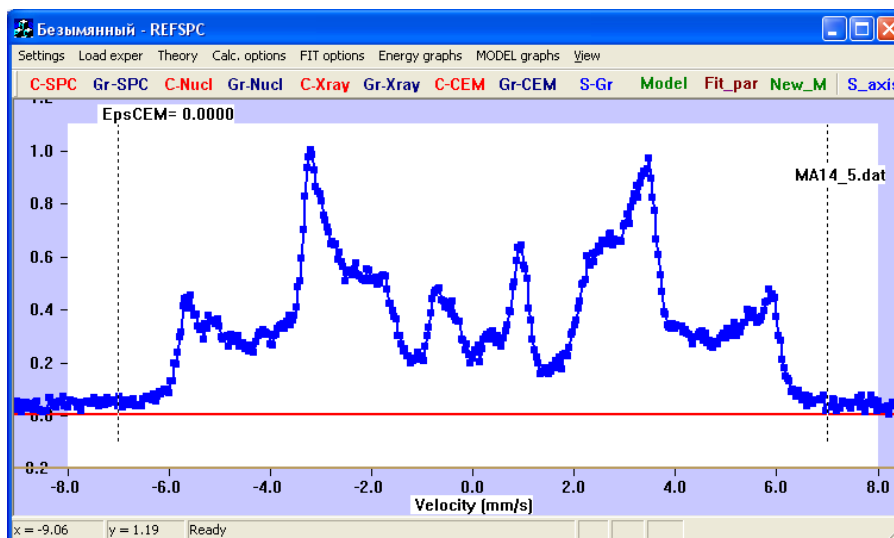

Fig. 7.

CALCULATION OPTIONS

Calculations can be performed if the needed *.exe files are presented in the used directory. The list of the *.exe files can be specified in the "**EXEC.INP**" file, which can be opened from the main window by "**Settings**" → "**Executable files**".

Calculations can be done if the model file is presented in the used directory, you can change the model file by "**Theory**" → "**Model file**". In the opened dialog you can change as well the number of the calculated reflectivity spectra and the values of the grazing angles for which the calculations will be done.

The calculations can be done with the help of the hot-keys buttons: **"C-SPC"**, **"C-Nucl"**, **"C-X-ray"**, **"C-CEM"** and after that the graphs with the results appeared.

"**Calcul.INP**" file.

You can change the parameters of the computations of the Mössbauer spectra of reflectivity in the "**Calcul.INP**" file (It opens by "**Calc. options**" → "**Energy spectra**"). You can choose the type of computation algorithm by the Jway=1 or 2 parameter (4x4-matrix or Parratt algorithm generalized to the anisotropic case). The Doppler velocity scale in the calculations should be determined by the **EMAXR** parameter and by number of points in the Mössbauer reflectivtity spectra (IMMR). The calculated spectra are convoluted with the line width of the Synchrotron Mössbauer Source (SMS). GSR parameter determines the half-width of the Synchrotron Mössbauer Source single-line.

The magnetic hyperfine field value can be described by some distribution. It can have the Lorentz or Gauss shape, or be determined by the external function given in "**DISTR.inf**" file. The choice is by the IDIST=1,2,3 parameter correspondingly. The number of points in the field distribution description is 2*JAV1+1, SD is the step of the normalized argument, so that for the field deviation ±DBHF(K) from the center of the distribution BHF(K) this argument is equal ±1.

The HFI nuclear density depth-distribution can be smoothed over several adjacent sublayers (regularization condition) along the Gauss profile, in this case the calculation parameter SIG determines the width (A) of the Gauss regularization, KP is number of steps in smoothing.

The computation JFIT parameter allows you to choose the type of the MERIT functions (they are described below). Then you can choose the interval on the energy scale, where the numerical comparison of the experimental and theoretical data will be done (from XEXP1 to XEXP2). We can fit several Mössbauer spectra of reflectivity simultaneously, in such case the MERIT functions are summed up with given weights for each Mössbauer reflectivity spectrum in consideration. This option gives a possibility to get the better improvement of the selected spectra during the fit. Ab initio the weights are 1 for each spectrum. The computation EPFIN parameter points out the limit of the improvement of the MERIT function for each model parameter variation after which we go to the variation of the next model parameter. AF gives the initial constant background in counts which later will be fitted, if AF=0 we do not take into account and do not fit the background. ITEST= 1 or 2 for one step check or for the fit in order to choose the best value of the parameter in consideration (the list of the varied parameters will be described below). ISTOP determines the maximum number of steps for the variation of each model parameter in the "consequent one-parameter descending" fit.

The correlation of the model parameters during their variations can be included: ICORR1 parameter points out the number of column (ip1) in which all model parameters will be changed simultaneously, if ICORR1 is negative it points out the number of line (in1) in the list of varied model parameters. Parameter IMAN1 (IMAN1 = 1,2,3 or 4) determines the way of correlation for this column (or line): IMAN1=1 means that all values in the column (line) are equal, IMAN1=2 means the equal steps, IMAN1=3 means that the steps are proportional to the value of the model parameter, IMAN1=4 means that the value of the model parameter is proportional to the old value. If ICORR1=0 and IMAN1=0 you have no correlations. It is possible to use up to 5 correlation conditions for different columns (lines) simultaneously. Such correlation of the parameters are helpful e.g. in the case if you apply a rather high magnetic external filed and all values of total BHF(K) should be decreased simultaneously, or if you consider the connected rotation (parameter GA(j)) of the $\mathbf{B}_{hf}$ in all layers under the action of the external field.

"**Refl.INP**" file

The parameters of the computations of the X-ray and nuclear reflectivity curves can be corrected in the "**Refl.INP**" file (It opens by"**Calc. options**" → "**X-ray and Nuclear refl**"). The parameter IntexpP (or IntexpD) = 0 means that there is no experimental data, IntexpP (or IntexpD) = 1 means that the comparison with the experimental angular dependencies is supposed for X-ray and nuclear reflectivity correspondingly. The names of the experimental data files should be on the next lines. The calculation parameters now are pointed separately for the X-ray and nuclear reflectivity curves, because the calculation time for the nuclear reflectivity curve is much longer than that for the X-ray curve. UT0p, Ustepp, Nstepp and UT0, Ustep, Nstep parameters are the initial angle, step and the number of points for the X-ray and nuclear reflectivity curve calculations respectively. JFITP and JFITD are the types of the MERIT functions (see below) for comparison of the theoretical and experimental curves. ACOMP1, ACOMP2 and ACOMP1D, ACOMP2D are the limits of the angular range where the comparison of the theoretical and experimental curves will be evaluated numerically (the X-ray and nuclear reflectivity curves respectively). EPFINP and EPFIND are the limits for iterations of the MERIT function. FJEPP and FJEPD are the weights of the **MERIT** functions for the comparison of the theoretical with the experimental curves of the X-ray and nuclear reflectivity. X-ray reflectivity angular dependency is calculated every time when you calculate nuclear reflectivity, but you can fit just the nuclear reflectivity if you put for example FJEPP=0. For the description of the experimental cut of the reflectivity at small grazing angles, the angle (ANGBEAM, mrad) should be determined at which the surface completely overlaps the beam. The DIV parameter characterizes the divergence of the beam (mrad) which will be used for convolution of the theoretical angular curves (this parameter is the same for both reflectivity curves). The DcorrIniP, DcorrIniD parameters determine the initial step for the X-ray angular scale correction (mrad). The necessity of such correction is forced by the fact that the experimental angular scale has often a great uncertainty in the zero angle determination. If DcorrIniP, DcorrIniD are 0, no correction will be performed.

When SMS is used, the nuclear reflectivity angular dependence is measured by integrating over Mössbauer spectra of reflectivity at each angular point. The last 3 lines in the "**Refl.INP**" file determine Emin ÷ Emax - the interval of Doppler velocities in which the nuclear reflectivity curves should be calculated and integrated, stepI parameter is the number of points for the Mössbauer spectra of reflectivity calculations.

"**CEMS.INP**" file.

The "**CEMS.INP**" input file gives the calibration data for the experimental CEMS spectrum (if it is given) and the calculation options for the theoretical CEMS spectrum. It is supposed that this spectrum is measured (and calculated) in normal geometry from the same sample from which the grazing incidence reflectivity has been measured. The first integer number NSPCE number can be 1 or 0 depending if you have the experimental data or not. Then GS parameter is a half-width of the source line (for convolution of the theoretical spectrum), EMAX is a maximal energy half-interval in calculations, IMM is number of points for calculation of the CEMS spectrum. After a blank line the name of the file with the experimental data file should be presented (on default it is "xxxC.dat"). In the next lines the information needed for calibration of the experimental data should be presented: JEXPC is the number of experimental points (max 1024), Hmms is the field in α-Fe in mm/s, Hchan is the field in α-Fe in channels and chan0 is the number of channel for zero velocity. Channel graduating value in mm/s is Hmms/Hchan. The numbers E1lim and E2lim are the limits in the velocity scale (in mm/s) where the comparison of the experimental and theoretical spectra

will be evaluated numerically. The last JFITC parameter determines the MERIT function for the comparison of the theoretical and experimental CEMS spectrum.

VARIATIONS of the MODEL PARAMETERS

The calculated spectra depend on the enormous amount of the structure and HFI parameters. If you want to follow the influence of each parameter on the spectra you can just open the model file by "**Theory**" → "**Corrections** " or by the hot-key "**Model**", change the selected parameter and make calculations by **"C-SPC"**, **"C-Nucl"**, **"C-Xray"** or **"C-CEM"**. You can see in the graph simultaneously the initial (first one for the session) theoretical spectra (thin lines) and the new one (thick lines): solid red lines are for the Mössbauer spectra of reflectivity and X-ray reflectivity, or blue curves are for nuclear reflectivity. Such simple way of the parameter variations are very helpful for understanding which one leads to which changes of the theoretical curve.

In the presented version of the REFTIM pack there are possibility to perform the automatic fit over the set of the parameter by several algorithms. the consequent one-parameter descending can be performed by "**SpecRef.exe**", "**RefNucl.exe**" , "**RefXray.exe**" and "**CEMS_S.exe**" executable files (which are determined in "**EXEC.INP**") for different curves. The Nelder–Mead method or downhill simplex method (AMOEBA method) is implemented in "**SpecR_Am.exe**", "**SpecR_Am.exe**", "**RefX_Am.exe**" and "**CEMS_Am.exe**" executable files. For the X-ray reflectivity curve the "**RefX_NET.exe**" file perform the calculations for the multidimensional net of the parameters with sequentially decreasing dimension of the net cell. (This method of fitting is possible to use because this kind of calculations is very fast).

Automatic fit needs determining the set of the parameters. For this purpose two numbers have assigned to each parameter in the model and these numbers for the parameters which you are going to test during the fit should be listed in the "**Next.inp**" file. The sequence of the fitted parameters in the "**Next.inp**" file can be determined by the "**FIT options**" → "**List_par**" buttons. This action creates and opens the file "**List_par.txt**" in which all parameters which are possible to vary are listed.

Each parameter in the opened file is characterized by the two numbers, which are written at the beginning of each line. They are the number of layer (the numbering is from the surface to substrate) or the number of HFI parameter and the type of the parameter (e.g. second number 1 means the thickness of the corresponding layer, 2 means the real part of susceptibility etc.) or the number of HFI. The third column in the file "**List_par.txt**" gives the value of all these parameters in your model. If you print the nonzero 4th number in the line of the chosen parameter, you select this parameter for the fit and the printed number determines the initial step in variation of this parameter. It can be up to 50 chosen parameters for fit by AMOEBA algorithm, 10 chosen parameters for fit by the NET method, and any number of parameters for the consequent one-parameter descending. When you close "**List_par.txt**" with saving the corrections, the "**Next.inp**" file will be created automatically. You can open it by by "**FIT options**" → "**Check list**" or by the hot-key "Fit_par". If "**Next.inp**" file contains some nonzero lines (some parameters are chosen for the fit) the executable files will work with these chosen parameters for their fitting, but in this case when you press **"C-SPC"**, **"C-Nucl"**, **"C-X-ray"** or **"C-CEM"** the program will ask you if you really want to perform fit (the dialog suggest you to mark the box) or you want just to perform the calculation for the given MODEL.

The last 3 numbers in each line of "**List_par.txt**" file (and "**Next.inp**" file) give the possibility to connect the variation of the chosen parameter with the variation of the additional parameter. By default they are 0 0 1.0. That means that there is no correlated variation. Two

integer numbers designate the connected parameter. The last number is the factor multiplying the step of the first parameter variation for the obtaining the step for the variation of the connected parameter. If this last number will be –1.0 the variation of the connected parameter will be opposite to the variation of the first parameter. It is important e.g. when you would like to change the thickness of one layer in the period, but you want to keep the value of the period.

The "**Next.inp**" file is opened by the hot-key "Fit_par". If you directed no parameters for fitting (or ab initio) this file contains just two lines, the first one is 1 and the second line is six 0 numbers. (This 0 line should end any sequence of lines in "**Next.inp**".)

It is recommended to look at the obtained "**Next.inp**" file (by "**FIT options**" → "**Check list**" or by the hot-key "Fit_par") for some corrections. For example you can change the sequence of lines in order to change the sequence of the parameter variations or to repeat some lines or group of lines for the repetition of the previous fit etc. Remember that the last line in the "**Next.inp**" file should be six 0 numbers. For the NET method the "1" in the first line should be replaced by "3" or "5" or "7". These numbers determine the number of points for each parameter in the net.

Notice that if in the "**Calcul.INP**" file you have ITEST=1 you will have just one step check in the consequent one-parameter descending algorithms but not fit. An initio ITEST=2, so the fit will be performed. Notice as well that the AMPEBA algorithm does not like any correlations of the parameters which can be done during the fit procedure. With some correlation options it is better to use the consequent one-parameter descending algorithms.

By "**FIT options**" → "**Fitting**" → "**Spectra of reflectivity**" or → "**X-ray reflectivity**" or → "**Nuclear+X-ray reflectivities**" or → "**Joint_FIT**" or → "**AMOEBA JOINT FIT**" you have different options. This way for calculations differs from that determined by the hot-key "**C-SPC**", "**C-Nucl**", "**C-X-ray**" or "**C-CEM**" buttons. Here you can follow the intermediate results by pressing the "Gr-SPC", "Gr-Nucl", "Gr-Xray", or "Gr-CEM" respectively. In addition it is possible to perform the joint fit of the Mössbauer spectra of reflectivity and reflectivity curves by two algorithms: consequent one-parameter descending and AMOEBA ("**Joint_FIT**" and "**AMOEBA JOINT_FIT**"). If you use this buttons for computation you should press pressing the "Gr-SPC", "Gr-Nucl", "Gr-Xray", or "Gr-CEM" buttons at the end of fitting procedure.

The fit of any curve can be initiated simply by the hot-key "**C-SPC**", "**C-Nucl**", "**C-X-ray**" or "**C-CEM**" and by marking the box in the dialog window. The final result appears on the screen automatically.

When the fit has been finished the old and new value of the MERIT function appears in the upper-left corner of the screen. The new model file will be created, it is "**LAYSPC.RES**", you can view it by the button "New_M". It is recommended to save this new file under the new name, as provided by the suggestion, and to point out this name as the model file for future calculations.

Notice that there are a lot of other options for correlation of the parameter variations which expand the possibilities of the program REFSPC. They are:
♦ the correlation between parameters in each layer or for each type of parameter,
♦ the normalization of the HFI distribution on the maximum density of nuclei in the structure or in each layer,
♦ the normalization of each HFI relative weight (when you can compare with e.g. multiplet areas in the absorption spectrum),
♦ the smoothing of the depth distribution functions for each multiplet or for all multiplets,

♦ you can attribute the angles of the HFI orientation for a given layer or to the given multiplet.

MERIT FUNCTIONS

For the dependencies which you prefer to watch in logarithmic scale the choice of the MERIT function is not simple. In order to enhance the contribution of the "tails" of the curves to the mean-square deviation of the theoretical dependence from the experimental one it was suggested to use the different power **n** of the denominator of the MERIT function (We designate it as EPS on the screen):

$$\text{EPS} = \sqrt{\sum_{i=1}^{N} \frac{(y_i - t_i)^2}{y_i^n}} \Big/ \sqrt{\sum_{i=1}^{N} \frac{1}{y_i^n}} \tag{1}$$

where n=1, 2, 3 … and respectively JFIT=1., 2., 3., ….. (or JFITP, JFITD, JFITC) for the choice of the MERIT functions in "**Calcul.INP**", or "**Refl.INP**", or "**CEMS.INP**". In (1) y_i and t_i are the values of the normalized experimental and theoretical points on the graphs, N is the number of points in comparison. For the Mössbauer spectra of reflectivity or conversion electron yield it would be better to use the usual mean square deviation i.e. JFIT=1.0.

In the paper [A.Segmuller, Int.conf. "Modulated structures", New-York,1979. p.78-80] an another criteria were used for the fit of the reflectivity curves. The specific feature of such dependences is the great amplitude of the function variations (up to 10^7). According to this paper we suggest also to use the following MERIT functions.

$$\text{EPS} = \frac{1}{\sqrt{N}} \sqrt{\sum \frac{(y_i - t_i)^2}{(y_i + t_i)^2}} + \sqrt{\frac{\sum(y_i - t_i)^2}{\sum y_i^2}} \,, \quad \text{JFIT=11.} \tag{2}$$

$$\text{EPS} = \sqrt{\frac{\sum(y_i - t_i)^2}{\sum y_i^2}} \,, \quad \text{JFIT=12.} \tag{3}$$

$$\text{EPS} = \frac{1}{\sqrt{N}} \sqrt{\sum \frac{(y_i - t_i)^2}{(y_i + t_i)^2}} \,, \quad \text{JFIT=13.} \tag{4}$$

You can see that JFIT=13.0 adjusts preferably the "tails" of the curves, JFIT=12.0 adjust better the largest part of the curves. The most suitable results in many cases we got with the function, corresponding to JFIT=11.0.

One additional JFIT=0.0 option is possible. It is the comparison of the experimental and theoretical curves in the logarithm scale:

$$\text{EPS} = \frac{1}{N} \sqrt{\sum_{i=1}^{N} (\log(y_i) - \log(t_i))^2} \,, \quad \text{JFIT=0.0.} \tag{5}$$

The choice of the criteria depends on the character of the curve. We can choose the MERIT function by comparing the influence of the different MERIT functions on the quality of the obtained result.

RESULTS

After each calculation or fit procedure the new model file "**LAYSPC.RES**" is created corresponding to the best obtained result for the varied parameters. You can look and save it for the memory or for the next calculations by the button "New_M". You can watch also on the graphs of the last obtained electronic density depth distribution and photoabsorption compared with the initial ones by "**Model graphs**" → "**El density"** or the obtained and initial depth distribution of HFI nuclear density for each multiplet by "**Model graphs**" → "**HFI graph**". The energy dependencies of the nuclear resonant spectra of absorption (at grazing angle) or reflectivity is presented by "**Energy spectra**" → "**Absorption**" or → "**Reflectivity**".

After each calculation by **"**C-SPC**"** button the following files are created : "**BUFFsp1.RES**", "**BUFFsp2.RES**", … for Mössbauer spectra of reflectivity (first column is the Doppler velocity, the second column is the experimental count, which is "0" if you have no experimental data, the third column is the superimposed theoretical curve) calculated at each chosen grazing angle; "**BUFFEN1.RES**", "**BUFFEN2.RES**", … files for the theoretical Mössbauer spectra of reflectivity (first column is the Doppler velocity, two second columns are the reflectivity for s- and p- incident polarizations) for the same grazing angles; "**E_spcN.res**" are the Mössbauer spectra of absorption at the " 0" grazing angle for two polarizations of the incident radiation; These spectra appear in the main window and in the additional widows "**Energy spectra**" → "**Reflectivity**" or → "**Absorption**" respectively. The "**EnerTest.res**" file presents the Mössbauer reflectivity spectra for p- and s- polarizations of the incident and reflected radiations respectively at the first grazing angle of calculations. The "**EL_mod.RES**" files gives the depth profile graphs of the Real and Imaginary parts of susceptibility in units of 10^{-6} used in the model, used in the calculations. These data are visualized by "**Model graphs**" → "**El density**". The file "**MODELN.RES**" gives the depth profiles of nuclear density characterizing by different kinds of HFI (normalized to the nuclear density in α -Fe), appeared by "**Model graphs**" → "**HFI graph**". The values of the last MERIT functions for each spectrum and their sum (appeared in the top left corner of the main window) is given in the "**RESULT.res**" file. The values of the last grazing angles, used in the calculations of the reflectivity spectra, are given in "**ANGLE.RES**" (this data are needed if the values of the grazing angles have been adjusted during the fit), the old angles are kept in "**OLD_ANG.RES**" file.

The angular dependencies of the reflecitivity are presented in the "**PROMP2.res**" and "**N_Refl.res**" for the X-ray and nuclear resonance reflectivity respectively (first column is the angles in mrad, the second column is the experimental count, , which is "0" if you have no experimental data, the third column is the superimposed theoretical curve). For the X-ray reflectivity the "**RELAY.RES**" file gives the absolute calculated curve (the non-normalized and non-averaged) of the reflectivity. The "**RESULTI.res**" file gives the merit function values for the fit of the X-ray, nuclear reflectivity curves and their sum. The "**INT_Nucl.res**" file contains the theoretical nuclear reflectivity curves for p- and s- polarizations of the incident and reflected radiations respectively (remember that that is the normalized integral over some spectral interval determined in "**Refl.INP**").

The "**CEMfit.res**", "**CEMorig.res**" files presents of the results of the CEM spectrum calculation for the normal incident and for the unpolarized radition or fit for the same model which have been used for the grazing incidence spectra. Notice that sometimes the models are not the same for the grazing incidence reflectivity spectra and CEMS if the experimental results have been obtained at different conditions: at different temperatures, at different external magnetic fields etc. The columns in "**CEMfit.res**" present the velocity, normnalized to "1" exper.data ("0" if you have no them), superimposed experimental curve and then the

multiplet contributions respectively. The "**CEMorig.res**" file contains the same data but conventionally normalized on the background (for following presentations). The files "CEMS_St.res" and "CEMS_At.res" contains the theoretical Mössbauer conversion electron spectra (normalized) with multiplet contributions.

At each calculation by "***.exe**" file the control parameters of computations are placed in the corresponding "***.res**" file.

SOME ADDITIONAL GRAPH OPTIONS

The right mouse button click activates the dialog window for the correction of the x-, y-scales and for the conversion of the spectra to the logarithm scale and back. The same option with **the right button** is valid for the "**HFI graph**", "**El. density",** "**Energy spectra**" → "**Absorption**" or → "**Reflectivity**"graphs. It is recommended to press "**S_axis**" button after each axis correction in order to save it for the consequent drawing.

When you are in the main window, **the left mouse button** click gives you the x- and y- coordinates of the point (in the left-bottom box).

Some limitations (but they could be easily corrected by request):

The maximum amount of the Mössbauer spectra of reflectivity (calculated for different angles) for simultaneous consideration is **4**.

The maximum amount of different HFI for ^{57}Fe nuclei in consideration is **8**.

The maximum amount of sublayers in consideration (without repetition) is **60**. After sub-division of the interfaces into several steps this maximum number could be **300**. The number of repetitions of chosen sequence of sublayers is arbitrary.

The **REFSPC.zip** pack includes two directories. In the "**ZERO**" you can try to make calculations if you have no any experimental data and you can try to create the model for calculations which you are interested in, following by "**Settings**" → "**Start from zero**". In this directory the "**Tconst.INI**" file and all *.exe files are presented. In the "**EXAMPLE**" directory you can test how the experimental data are treated following by "**Settings**" → "**Get previous settings**". The needed input files and examples of the experimental and model files are given in this directory in addition to all *.exe files which is possible to use.

Attention! Be careful during unpack: the program does not like the names of directories with blank spaces.

The program pack "**REFSPC**" has been created by Marina Andreeva (Mandreeva1@yandex.ru) on the basis of the previous program pack "**REFTIM**", created by Marina Andreeva with essential corrections made by Bengt Lindgren (Bengt.Lindgren@fysik.uu.se) and the very effective practical help by Vitalii Panchuk (vitpan@mail.ru).

The kind request
*If you have some questions or if you discover some mistakes, instability, misprints or other unclear moments in the program or in this program description **please inform us** by e-mail to:* **Mandreeva1@yandex.ru**