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M.SFINKS DIFFRACTOMETER AT GATCHINA REACTOR.

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ABSTRACT

Some details of design and technical parameters of the neutron Fourier diffractometer "M.SFINKS" installed at Gatchina (Russia) reactor are presented. Some achieved scientific results are presented also.

1. Introduction

The present time is characterized by the development of new technologies and new materials accordingly. In the next order this situation have stimulated the development of new methods and modernization of using ones especially nondestructive types. The diffraction methods based on penetrating rays are ones of the most significant in long list of such methods. The neutron diffraction is occupied very significant complementary niches to *x*-ray one. The main reason of this definition is a great advantage of the luminosity of *x*-ray sources. For compensation of this situation the creation of the powerful and perfect neutron sources is continuing in the world.

Design and construction of new high flux neutron sources have stimulated development of advanced instruments for carrying out research at these sources. A good example illustrating the above statement is the building of a high flux reactor at ILL (France) whose instrument suit costs much more than the expenditure of money on the reactor itself. This stems from the fact that reactors are expensive and one should take care of their most effective exploitation.

So the new Fourier diffractometer was designed for the steady state reactor PIK, the construction of which started in 1976 in the town of Gatchina (about 40 km south from St.-Petersburg) and is continued up to present time. By 1978 the list of instruments was formed for the realization of the research program being developed for this reactor. It included a number of diffractometers for experiments with powder samples. By that time became known successful applications of the Rietveld profile analysis method [1] and high resolution diffractometers [2,3]. This tendency in neutron diffractometry development and application received confirmation in a detailed consideration of the bright prospects opening with the use of high resolution neutron powder diffraction methods [4].

Keywords: Neutron, Diffraction, Structure properties

In 1979 during the visit of Prof. P. Hiismaki to the Petersburg Institute of Nuclear Physics in Gatchina a decision was reached to build a Fourier diffractometer at the steady state reactor PIK. During the 1980 year design plans and specification were executed. This file of documents were submitted for approval of the experts from the United Kingdom, Norway and Sweden and being given it. The work started on design of particular units and elements of the diffractometer.

To the greatest majority of improvements was subjected the electronic system. The one that served the diffractometer model in Finland [5] executed a successive mode of signal transferring with a very large dead time and could not be used with high intensity beams. Therefore, a new analyzer was to be designed operating in a parallel mode of signal transferring. Two versions were considered: a multicomputer and a microprocessor system. The latter one has won the competition. Special chips with internal logic were created. Now we use a 32-channel one for building the analyzer. By 1983 we were ready to start assembly of the new diffractometer on a neutron beam. However, as the completion date of the PIK construction was postponed to after 1986 acuteness became the question of what to do with the newly built equipment. After long and difficult discussions it was decided to install it on the old reactor. In 1984 works started on the preparation to operation of this new diffractometer "M. SFINKS", the given name, on beam 9 of the WWR-M reactor at Gatchina [6]. On Fig.1 the scheme of this diffractometer and steps of its modernization are presented. Its upgrading was finalized with the installation of a four-element neutron detector schematically shown in Fig.2. The surfaces of the converters (lithium glass elements pasted on light guides) were adjusted most close to the time focusing geometry. The time-focusing conditions are defined by the following formula:

$$b(\theta_B) = \frac{(a+b_0)}{\sin\theta_B} - a \quad ,$$

a - distance chopper-sample

$b(\theta_B)$ - distance sample-points on the time focusing surface.

b_0 - distance sample-time focusing surface when $\theta_B = 90°$.

The aperture of the detector was 0.09 sterad.

As is seen on Fig.1 the "M.SFINKS" diffractometer is machine with fixed geometry the mostly matched to structural investigations of materials under extreme conditions being included in the scientific program of reactor PIK. Also such instruments are giving the general preference in realization of structural studies as they are capable of providing more rich uncorrelating experimental information for the application of the Rietveld method. The distance between uncorrelating points in the diffraction spectrum is defined by the resolution of the instrument.

This is conditioned by the shape of the dispersion curves $\Delta d/d_{hkl} = f(d_{hkl})$ for the time-of-flight technique and the constant wavelength method. They are illustrated in Fig.3. As is seen from this figure the time-of-flight method covers with high resolution a much wider range of d_{hkl} (interplane spacings) than the constant wavelength method does. Figure 3.1 shows the resolution function of the time-of-flight diffractometer of M.SFINKS installed at the WWR-M reactor at Gatchina. Figure 3.2 illustrates the resolution function of the multidetector diffractometer D1A (ILL, Grenoble), which immediately followed by questions of its selection.

The time-of-flight diffractometer requires time-dependent periodicity of the steady state neutron intensity and its main parameters (resolution, luminosity, geometrical size) depends on the time characteristics of the beam.

There are several ways of producing pulsed neutron beams at steady state reactors. The most popular is the use of mechanical systems (choppers). The chopper consists of two parts. One of them is the fast rotating disk (rotor) and the other is a fixed element (stator) with one or more neutron opaque slits. In the periphery of the rotor in some way or another there are also made neutron opaque slits. If these slits are arranged with some periodicity the chopper is called the Fourier chopper. If the arrangement of these slits is random, the chopper is called the pseudo-random chopper. The one with few (2 or 4) equidistant slits in the periphery of the rotor has got the name of the Fermi chopper. There exist other methods for pulsed neutron beam production, but they are not the topic of the present paper.

From the viewpoint of the main parameters of diffractometers (luminosity and resolution) the Fourier and pseudo-random versions are equivalent. However, it is cheaper to build a Fourier and pseudo-random techniques one needs some special procedures to be performed to restore the studied spectrum. The Fourier and pseudo-random techniques are efficient in measuring spectra with well pronounced lines. Spectrum refinement with a Fourier or pseudo-random method requires exact knowledge of the phase of the neutron wave passing through the chopper. This is the principal problem the solution of which determines success of practical realization of these techniques.

2. Diffractometer "M.SFINKS" - ideas and realization

This solution was found and tested by the group of Prof. P Hiismaki at VTT (Finland). They have developed the so-called Reverse Time-of-Flight Fourier Method. What does this method consist in Figure 4 gives schematic illustration. The scheme comprises the Fourier chopper, the detector, the phase shifting register, the transferring logic unit and the analyzer. The Fourier chopper performs time modulation (Fig.4) of the beam described by the function:

$$x^w = \sum_1^\infty p_r e^{irwt}$$

where p_r are corresponding Fourier coefficients.

The detector intensity $Z^w(t)$ can be given at each rotation speed as integral over time-of- flight span T_s where the scattering cross sections of samples give non-zero contribution:

$$Z^w(t) = \int_0^{T_s} S_0(\tau) x^w(t-\tau) d\tau + b_0$$

where b_0 - describes the unmodulated background.
$S(\tau)$ is the time-of-flight primary spectrum incident on the sample. $S_0(\tau)$ is convolution of the primary beam spectrum incident on the sample and scattering function of the sample. The rotor rotation frequency changes following $G(w)$. This function must satisfy the condition $G(w)dw=dt$, that determines the time interval dt

within which the frequency changes from w to dw. The frequency is changed from 0 to w_{max}. The function $G(w)$ is normalized to unity, i.e.

$$\frac{1}{T^{w_{max}}}\int_0^{w_{max}} G(w)dw = 1$$

The total time for running the chopper from 0 to w_{max} is marked by $T^{w_{max}}$, then the time spent near the speed w is given by $dT^w = G(w)dw$.

A device is mounted on the chopper to generate a pick-up signal, e.g., in the form of a rectangular pulses. This signal is also described by the Fourier series expansion:

$$y^w(t) = \sum_{r=-\infty}^{\infty} q_r e^{irwt} \quad .$$

The pick-up signals come to the shifting register, through which they are step-wise transmitted with step period Δ by a special generator, that synchronizes the work of all electronic systems. Phase determination accuracy in the shifting register depends on stable operation of this generator and the value of the step period Δ. This is the principal moment hard to be accomplished in the direct method. Such a distribution of phases from the shifting register comes to the analyzer via the transferring logic unit at the moment of neutron registration by the detector. Thus the transferring probability is proportional to the neutron intensity of the detector $Z^w(t)$ and accumulated data in the analyzer can be represented by help of following formula:

$$Z(\tau) = \int_0^{w_{max}} \Delta Z^w dw = C\int_0^{T_s} d\tau' S_0(\tau')R(\tau - \tau') + (S_0\bar{x} + B_0)\bar{y},$$

where

$$\Delta Z^w(\tau) = \Delta T\int_0^{T_s} d\tau' S_0(\tau')(\overline{xy} + 2\sum p_r q_r e^{irw(\tau-\tau')}) + b_0\bar{y}\Delta T^w$$

Here the bar indicates time average. As results

$$Z(\tau) = C\int_0^{T_s} d\tau' S^0(\tau)R(\tau - \tau') + (S_0\bar{x} + B_0)\bar{y}$$

The symbols have the following meanings:

$S^0(\tau) = T_m S_0(\tau)$, $S_0 = \int_0^{T_s} S_0(\tau)d\tau$, $B_0 = T_m b_0$,

T_m - the time of the measurement.

$$R = \frac{2}{C}\sum_{1}^{\infty} p_r q_r G(rt) .$$

$$G(t) = \int_{0}^{w_{max}} G(w)\cos(wt)dw$$

The function $G(t)$ is the Fourier transformation of the frequency window. The function x, y, $G(w)$ can be selected so that R will have the form close to δ-function and its width will determine the resolving power of the instrument. Then $Z(\tau)$ will be the studied spectrum. A brief account of the technique and the possible ways of its realization can be found in [5] and a more detailed description [7].
Table 1 summarizes the technical parameters of the diffractometer after the last modernization in 1986 in comparison with the parameters of the analogous instruments.

Table 1

parameter	D1A, ILL	GPBD, Argone	M.SFINKS Gatchina	D2B, ILL	HRPD RAL, England
λ, Å	**1.2-6**	**0.5-6**	**1-5**	**1-6**	**1-12**
Φ_s, n/cm²sec	**$2\cdot10^6$**	**~10^5**	**$1.5\cdot10^7$**	**~10^7**	**10^6**
V_s, cm	**3**	**5**	**5**	**5**	**2**
R, %	**0.2**	**0.25**	**0.25**	**~0.05**	**0.05**
Ω, sterad	**0.004**	**0.1**	**0.09**	**0.008**	**0.1**
$\Phi_s V_s \Omega$	**$2.4\cdot10^4$**	**$5\cdot10^4$**	**$f_k\cdot6\cdot10^6$**	**$4\cdot10^5$**	**$2\cdot10^5$**

λ , Å - the wavelength range attainable in the experiment;
Φ_s , n/cm²sec - is the neutron flux at sample site;
V_s , cm - the maximum sample volume;
R , % - the resolution;
Ω , sterad - the detector aperture;
$f_k \approx 0.02$ - the effective correlation coefficient.

So installation of the M.SFINKS diffractometer on an average flux reactor is superior the DIA on the high flux reactor of ILL (old version). M.SFINKS test measurements were performed with standard samples $Zr_{1-\delta}$ Hf_δ O_2, recommended by the Crystallography Community Committee. Figure 5 shows the experimental spectrum and the difference with the theoretically calculated one. Table 2 lists the extracted parameters. They are in good agreement with the results of investigations performed at the other research centers.

Table 2

$Zr_{0.98}$ $Hf_{0.02}$ O_2 Sp. gr. $P2_1/c$ No.14 setting 2,
a= 5.1447(1), b= 5.2099(2), c= 5.3117(1), β=99.219.

Atom	Occupation	x	y	z	B_{iso}
Zr/Hf	0.98/0.02	0.2756(2)	0.0407(2)	0.2082(2)	0.12(1)
O1	1	0.0695(3)	0.3333(3)	0.3433(2)	0.33(2)
O2	1	0.4185(2)	0.7562(2)	0.4794(2)	0.16(1)

3. Review of scientific studies

From the structural investigations performed with the wide use of the isotopic contrast method emphasis should be laid on the following compounds:
$Re(DCOO)_3$, Re=Y, Ce, Sm, La, Tm [8, 9, 10];
$Re B_6$, Re=La, Ce, Nd, Sm, Y [11, 12, 13, 14];
$Re_2 Cu O_4$, Re=La, Nd, Sm [15, 16, 17];
$Re Ba_2 Cu_3 O_7$, Re=Y, Sm, Gd, Eu [18, 19, 20, 21];
1-2-4-type superconductors $Y_{1-x} Ca_x Ba_2 Cu_4 O_8$ [22, 23].

1. $Re(DCOO)_3$ list of compounds is rather interesting due to non-linear optical properties and its possible relation with structure. It was discussed some phases related with optical peculiarities, also it was discussed the changing of the optical properties along the list of rare earth-elements [8, 9].

As result of our studies we didn't observe significant structural difference in all list of formates from Y to Tm. Isostructural list was interrupted on Tm. We observed the hydrogen bonding in all isostructural list [8, 9]. We optimized the sensitivity of diffraction experiment by help of isotope "0"-matrix of Sm [10] for the study possible temperature changing in structure near temperature of decomposition which starts from Re-0-bonding. Some models of decomposition might be discussed.

2. The hexaborides in frame of long list of rare earth elements and Y are very interesting. Along this list it can be observed the different physical properties from superconductivity to Condo-behavior. We started from the problem of the distribution of vacancies in hexaboride structure. By help of using "0"-matrix of Sm [11] we have observed the location of the vacancies in boron sublattices. We have defined temperature dependence of Debay-Waller factor for both sublattice of hexaborides (Re and B) [12], also we observed the steady-state Debay-Waller factor and have fixed the type of thermal vibration model, Einstein model for Re-sublattice and Debay model for boron one [12, 13]. We calibrated "M.SFINKS" diffractometer by help single crystal x-ray measurements and neutron powder ones. We have observed a good correspondence between both methods, Fig.6. Also we observed the softening of the phonon acoustic mode along list rare-earth hexaborides [14]. Now we are starting the modeling of the dynamical properties of hexaborides using valence

force field method. On the first stage of such treatment we have a good agreement between experimental data and theoretical simulation. These results which confirmed high resolution of M.SFINKS diffractometer will be published soon.

3. The structure of $Re_2 Cu O_4$ was studied. We fixed phase-diagram of ortho-tetra transition for $La_{1-x} Sr_x Cu O_4$ compound by help of temperature dependence of the Bragg-peak splitting [15]. Also we observed some structural effects due to oxygen content[16]. In time of the study Sm_2CuO_4 it was observed the non - linear temperature dependence of the lattice parameter which might be related with a fluctuation of Sm valence. May be it is one of the main reason for explanation of the difference in T_c between $Nd_{1-x}Sr_xCuO_4$ and $Sm_{1-x}Sr_xCuO_4$ [17].

4. We have actively participated in research of high-T_C superconductive ceramics type 1-2-3. One of most reliable results concerning structure of Y 1-2-3-compound was achieved by help of study carried out on "M.SFINKS" [18]. We paid attention on some possible anomalous behavior of the structure of 1-2-3-compounds. We have optimized experiment by help of "0"-matrix of Sm and ^{63}Cu. We observed anomalous kink in temperature dependence of unit cell parameters near T_C [19]. Also we used this compound for the "M.SFINKS" calibration by help of direct comparison with D2B (ILL) and DMC (Villigen, Swizerland). Fe-Cu substitution was carefully studied in complex research by using of "M.SFINKS", D2B, DMC [20]. For systematic research of 1-2-3 compounds [21] Sm, Gd, Eu versions were attested on "M.SFINKS" diffractometer preliminary.

5. We have prolonged our collaboration with Villigen in the study of Ca-substituted 1-2-4-system [22, 23]. We have observed that the Ca substituted Y in structure [22]. Also phase transition near 155K was observed [23].

4. Conclusion

The numeral physical results to be achieved by help of "M.SFINKS" diffractometer have confirmed a high reliability of the developed method which might be recommended for wide using. Results reported in [21, 22, 23] were supported by Soros fund from the Russian side.

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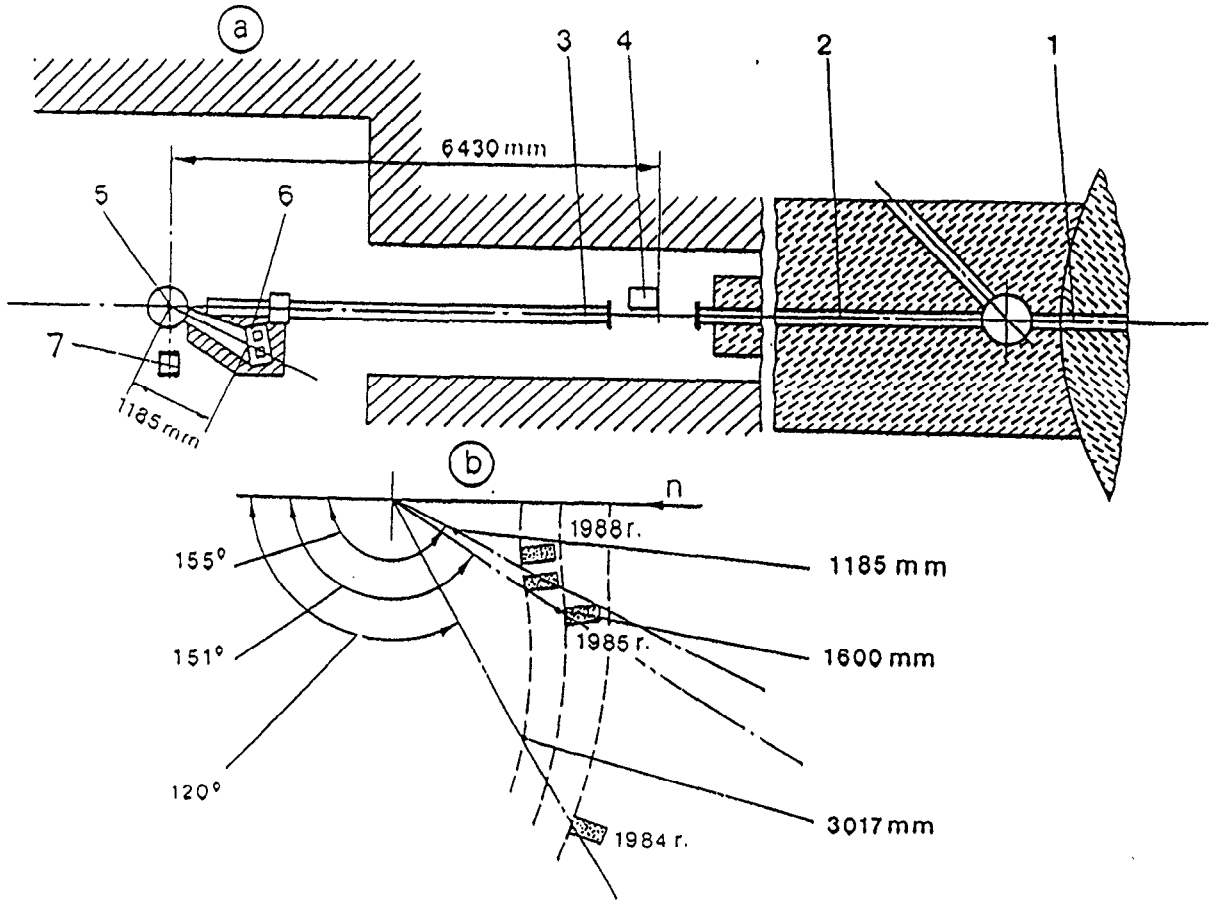


Fig.1 Layout of "M.SFINKS"-diffractometer and steps of its modernization.
1 - in-pile collimator, 2 - curved neutronguide, 3 - mirror collimator, 4 - Fourier chopper, 5 - sample position, 6 - back-scattering detector, 7 - 90^0-detector.

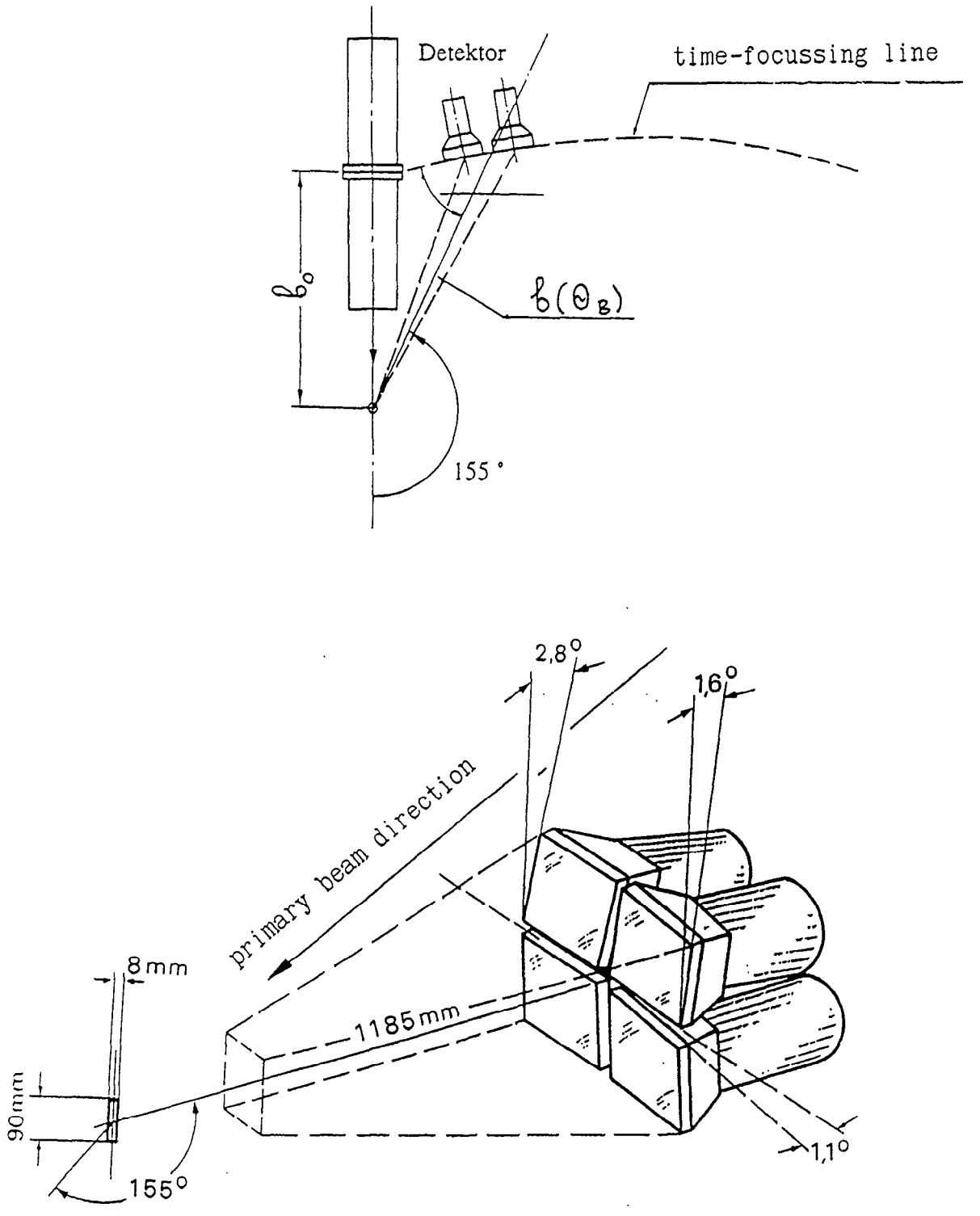


Fig.2 Scheme of the four-elements detector.

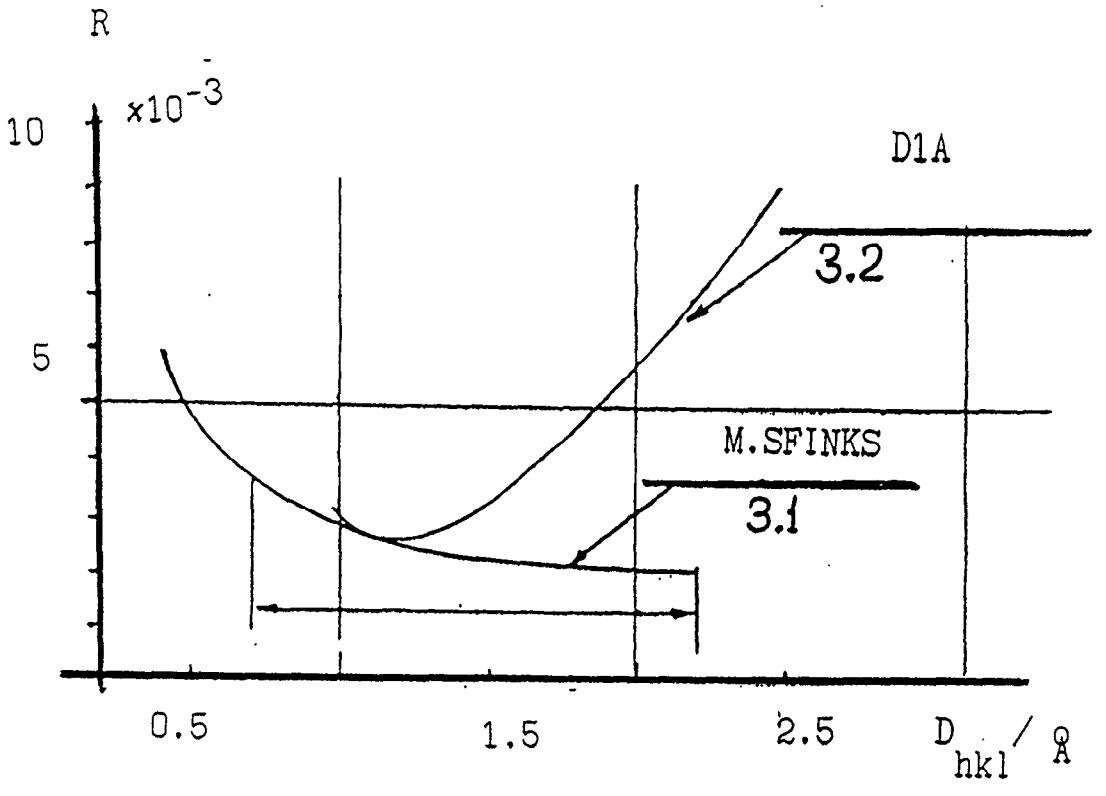


Fig.3 Resolution of "M.SFINKS"-diffractometer and D1A (old version, 1.909 Å).

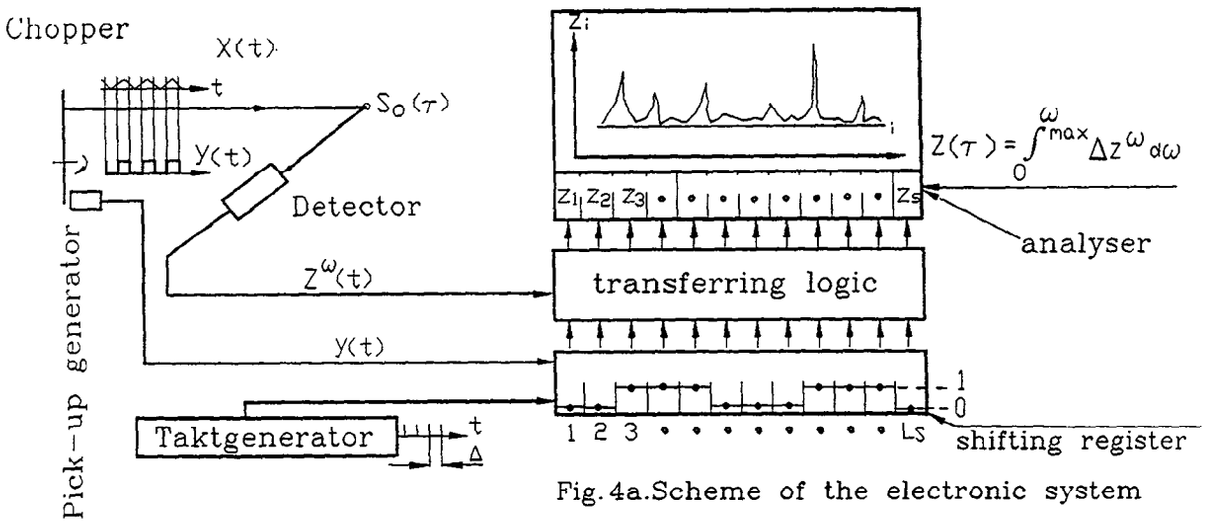
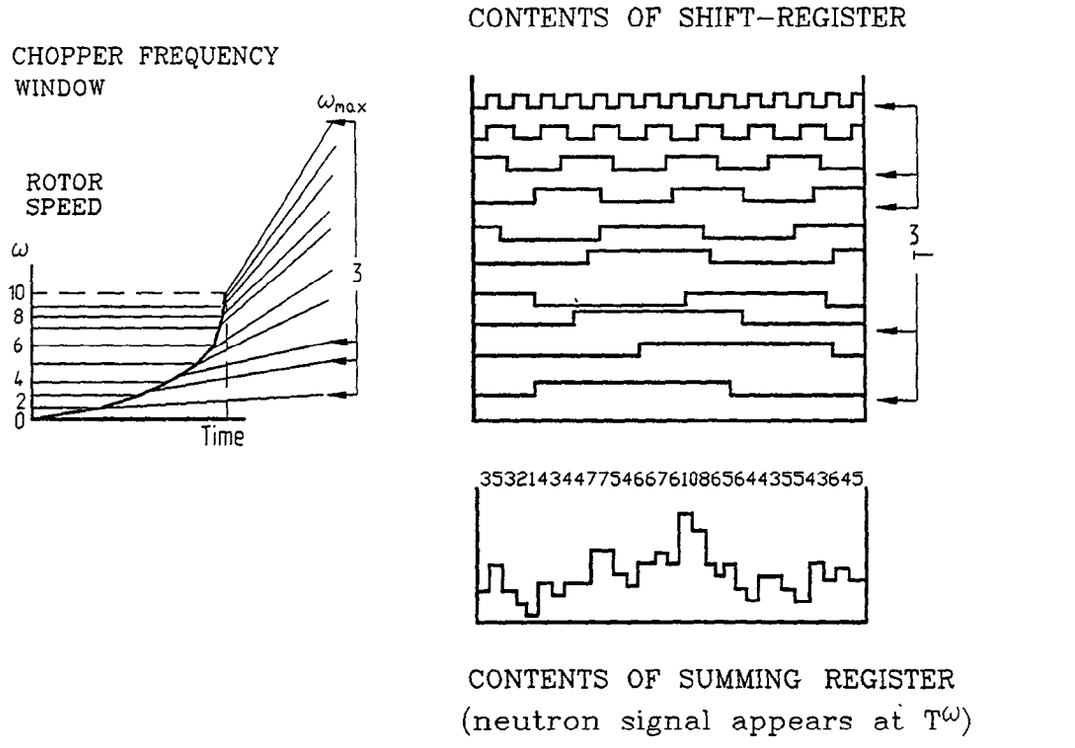


Fig.4a.Scheme of the electronic system



4b. Scheme of a synthesis of a diffraction spectrum by the reverse Fourier method.

Fig.4. Principal scheme of the spectrum registration of the "M.SFINKS" -diffractometer.

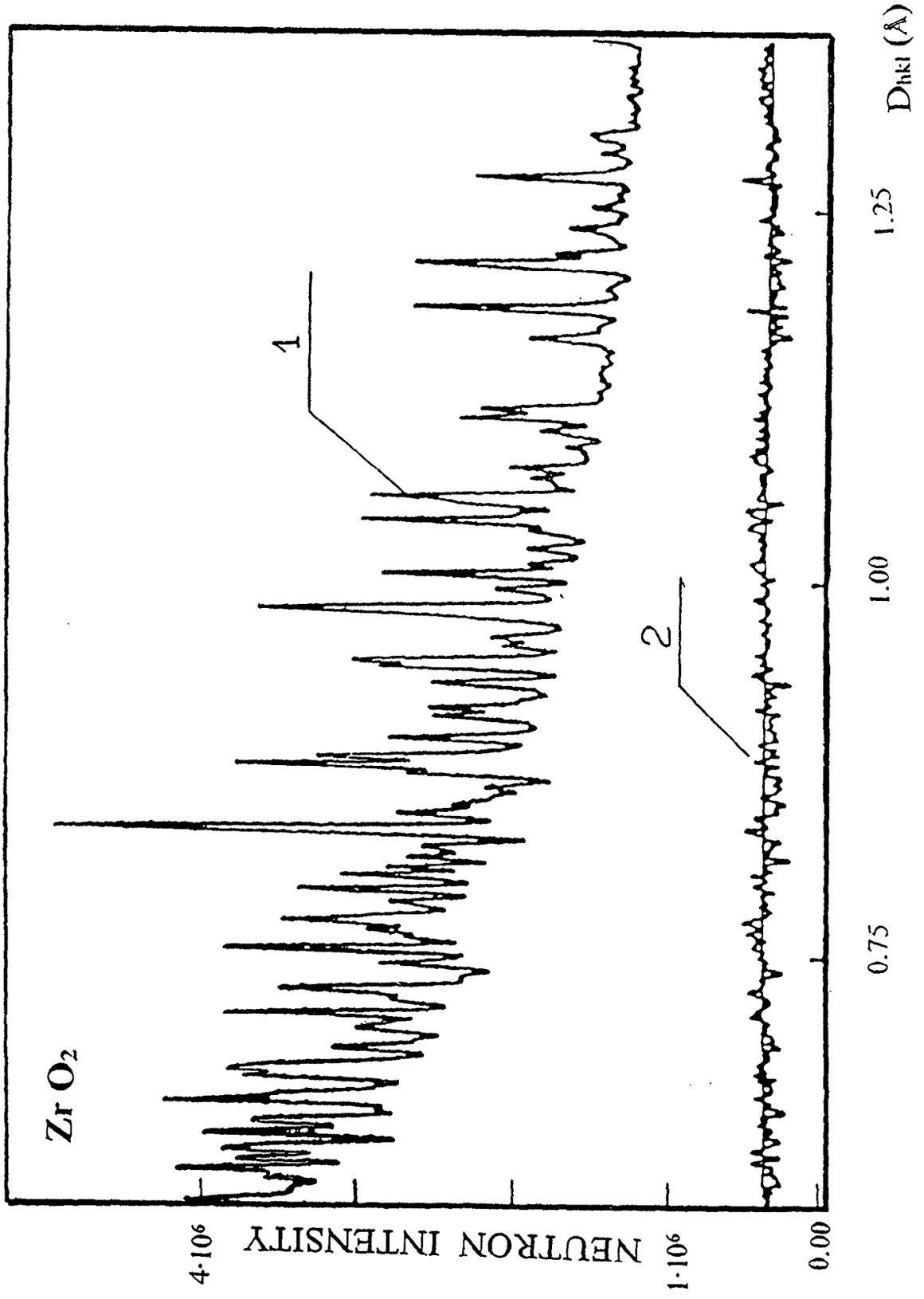
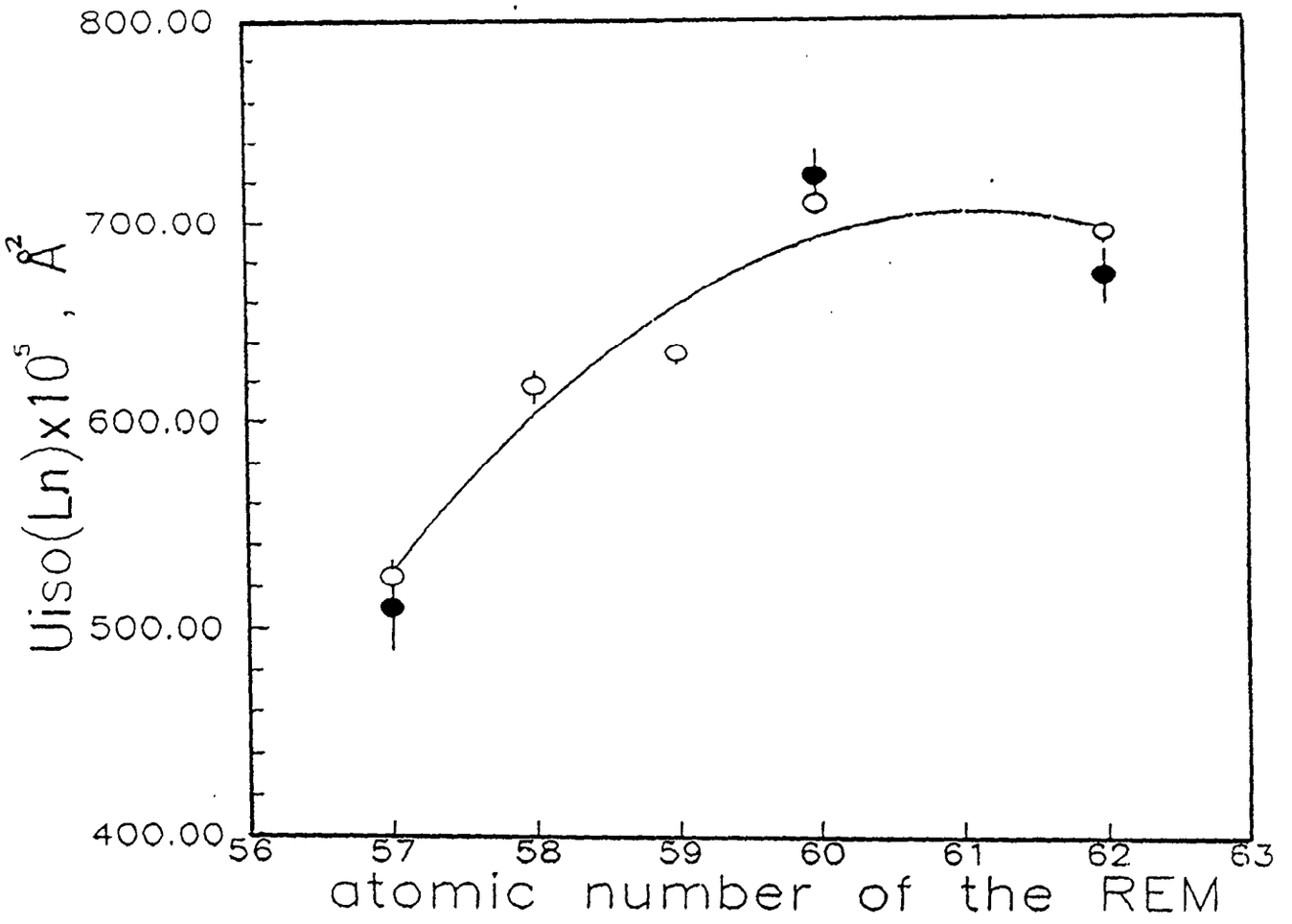


Fig.5 Diffraction pattern from $Zr_{0.98}$ $Hf_{0.02}$ O_2 sample (1) and difference experiment - computation (2).



○- defined from single crystal X-ray data

●- defined from neutron powder data

Fig.6 Isotropical thermal parameters of Re atoms. Neutron and *x*-ray diffraction data.