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### Neutron time-of-flight diffractometry

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<u>Abstract.</u> Neutron time-of-flight diffractometry provides an effective and rapidly developing method for current neutron diffraction studies. It has great prospects owing of the construction of new high-flux neutron sources producing either pulsed or continuous beams. The authors discuss specific potentialities of the method for structural studies. Special attention is paid to recently evolved lines of research including correlation neutron diffractometry, kinetic processes, the use of high pressure, external electric and magnetic fields.

### 1. Introduction

In order to understand the properties of condensed matter at the microscopic level, it is in the first place necessary to know how elements are organised in solids and fluids. The answer to this question lies in the atomic-molecular structure which can be established based on the wave diffraction patterns if the wavelengths are commensurable with the interatomic

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Received 29 May 1996 Uspekhi Fizicheskikh Nauk **166** (9) 955–985 (1996) Translated by Yu V Morozov, edited by L V Semenova distances. X-ray diffractometry is most extensively used for this purpose as a well-developed technique readily available in many laboratories. Recent progress in the construction of synchrotron radiation sources has further enhanced potentialities inherent in this method.

At the same time, solution of certain problems in crystallography using X-ray structural analysis encounters great difficulties and is sometimes utterly impossible with modern experimental techniques. These problems include, among others, localisation of light atoms surrounded by heavy ones, distribution of elements with close atomic numbers, isotope substitution and magnetic structures. Nor can these problems be solved using electron diffractometry.

In these and some other cases, the use of thermal neutrons may be of greater help [1-4] because their interaction with matter is of a totally different nature than that of X-rays and electrons. Neutrons interact with both nuclei and electrons (spin interaction). The nuclear scattering amplitude is determined by nuclear forces and does not decrease with increasing momentum transfer like the amplitude of X-ray or electron scattering. This allows for measuring higher scattering values and thus for more accurate location of nuclei. Moreover, the neutron scattering amplitude does not show as regular dependence on the atomic number as that of X-rays and electrons. Light elements such as hydrogen have relatively high scattering amplitudes which accounts for their being more readily 'exposed' by neutrons. Finally, the neutron scattering amplitude for isotopes of the same element varies considerably (up to sign reversal), in contrast to photon and

An important advantage of using neutrons in condensed matter studies is their interaction with the magnetic moments of atoms. Nowadays, neutron magnetic scattering and especially polarised beams are major sources of knowledge about magnetic structures.

It is worthwhile to emphasise that both nuclear and magnetic interactions between thermal neutrons and matter are relatively weak: neutrons do appear to appreciably affect the structure and chemical properties of matter as is for instance the case with photoemission. Therefore, the calculation of scattering cross-sections may be restricted to the first order of the theory of perturbations. Also, weak interactions account for deeper penetration of neutrons into the sample than that of X-rays and electrons which allows volume structural and dynamic effects to be examined.

Apart from the above properties of thermal neutrons, their wavelengths ( $\lambda = 1-10 \text{ A}$ ) and energies ( $E_n = 1-100 \text{ meV}$ ) correspond to the typical interatomic distances in solids and fluids as well as to characteristic excitation energies. Therefore, one and the same neutron source may be used to study both the structure and the dynamics of matter.

All these features of neutron-matter interaction have greatly facilitated the extensive use of neutron-based techniques, in the first place neutron diffractometry which is currently employed to characterise virtually any new compound. It is worth noting, however, that modern neutron sources are very expensive devices to be used only when no other technique is able to provide the desirable information. Moreover, previous certification of the sample is deemed necessary before experimenting on a neutron reactor, i.e. its characterisation by all other methods available starting from X-ray structural analysis.

Neutron diffraction was first reported to occur in three papers published in 1936 soon after the discovery of neutrons. However, the new phenomenon could not be used for practical purposes at that time because of low performance of the sources. In 1943, a graphite reactor producing continuous neutron beams was set working in Oak-Ridge, USA. In 1947–1948, C Shull and co-workers conducted the first structural experiments which provided the basis for the development of structural neutron diffraction. C Shull and B Brockhouse shared the 1994 Nobel Prize in Physics 'for their pioneer contribution to the development of neutron scattering techniques for the investigation into condensed matter' during 1947–1960.

From the very beginning, neutron diffractometry developed along the same lines as X-ray diffractometry by virtue of common laws underlying the two phenomena. However, marked differences in experimental approaches became apparent in the course of time. In accordance with the Bragg equation, there are two ways to obtain reflections from an atomic plane: by angular scanning of the spectrum at a constant wavelength (the constant wavelength or monochromatic beam method) and by wavelength scanning at a constant scattering angle (the constant angle or white beam technique).

In the former case principally realised with sources generating continuous neutron fluxes, the design of an

experiment is not substantially different from that in the case of X-ray diffractometry [1, 2]. In the latter case, a relatively low velocity of thermal neutrons facilitated the development of a new technique in which the wavelength scanning is virtually changed-over to the neutron time-of-flight scanning. Indeed, the wavelength of a neutron can be deduced from the de Broglie relation provided its time-of-flight is known. Analogous to the time-of-flight neutron diffractometry is the use of detectors sensitive to the energy of incident  $\gamma$ -quanta in experiments measuring diffraction of synchrotron- and X-radiation. The time-of-flight method in neutron diffractometry is most efficacious when pulsed neutron sources are available.

The time-of-flight method was introduced to neutron spectroscopy in 1935 when the first mechanical chopper of neutron fluxes was constructed [5]. P Egelstaff seems to have been the first to suggest the application of this method to crystal structure studies in his report at the 1954 World Congress of Crystallographers. He elaborated this idea in greater detail in Ref. [6], and it was further developed in Refs [7, 8]. An attempt to realise it at the 2 MW reactor at Swierk, Poland, dates back to 1963 [9] even though it was clear at that time that pulsed neutron sources are more adequate for the purpose of time-of-flight diffractometry. One of the first sources of this type for physical research (the IBR pulse reactor) was commissioned at the Joint Institute for Nuclear Research (JINR), Dubna, Russia, where it was from the very beginning used in studies employing the time-of-flight method [10]. Experiments on time-of-flight diffractometry with the IBR reactor were started in 1963; actually, they were the first real experiments in this field that confirmed validity of the method [11 - 14].

The first experiments at Swierk and Dubna were soon followed by a rapid spread of time-of-flight diffractometry to other laboratories [15]. In 1964, a time-of-flight diffractometer was installed at a steady state reactor at Riso, Denmark, equipped with a Fermi chopper [16]. Diffractometers similar in design were coupled with electron accelerators used as pulsed neutron sources in USA, 1966 [17], Japan, 1968 [18], and UK, 1969 [19]. Like the very first diffractometer of the IBR pulse reactor, these instruments provided greater opportunities for experimentation as compared with a steady state reactor – Fermi chopper facility. Nevertheless, they were far less efficacious in terms of luminosity than conventional double-axis diffractometers used at steady state reactors.

In addition, the time-of-flight method was shown to have obvious advantages, e.g. fixed scattering geometry, which made experimenters look for the ways to use it in conjunction with steady state reactors without a marked loss of neutron flux intensity. A rational approach that implied the use of a fast Fourier chopper was suggested in the USA in 1968. Methodological problems encountered in the restoration of the diffraction spectra in the experiments using Fourier choppers were resolved by Finnish physicists who developed the reverse time-of-flight technique [21, 22] and realised it in a model experiment at the VTT reactor in 1975. The first Fourier diffractometer for structural studies with a steady state reactor was constructed at the Institute of Nuclear Physics (PIYaF) Russian Academy of Sciences, Gatchina (near St Petersburg) [23]. In 1988, a similar instrument was used in combination with the GKSS reactor in Geesthacht, Germany [24]. The reverse time-of-flight method and Fourier diffractometers provided the basis for a new branch of neutron diffractometry.

The situation in time-of-flight diffractometry research changed dramatically after several pulsed neutron sources had simultaneously been constructed in different laboratories in the 1980s; those devices produced neutron fluxes with intensities one to two orders of magnitude higher than in reactors of the first generation. Therefore, the Eighties may be considered to have given second birth to time-of-flight diffractometry. During the next decade, each new neutron source was equipped with one or more time-of-flight diffractometers which were by no means inferior to their analogs used on steady state reactors and performed even better in terms of selected parameters.

Another breakthrough in time-of-flight diffractometry was the construction in 1992 at the high-flux pulsed reactor IBR-2 in Dubna of a high resolution Fourier diffractometer, currently ranked among the best in the world [25-27]. The experience with this first Fourier diffractometer on a pulsed neutron source indicates that time-of-flight diffractometry is on the brink of further progress having in prospect the construction of new Long Pulsed Sources (LPS).

After having worked its way via a few stages of the development, time-of-flight neutron diffractometry came to be considered a valuable technique for current neutronographic research. Its further improvement depends on the construction of high-flux neutron sources of the next generation.

The present review updates the reader on the present-day usage of time-of-flight diffractometry and its prospects in the near future. The review is intended for specialists in different fields of natural science, viz. physicists, chemists, biologists, and experts in the science of materials who use or wish to use neutrons in their structural studies. Special attention is paid to those methodological problems which have not been properly highlighted in other reviews and monographs. Fundamentals of neutron diffractometry are expounded in Refs [1-3].

### 2. Modern neutron sources

Intensive neutron beams are produced via nuclear reactions involving photoneutrons, evaporation, and fission of heavy nuclei [28]. Nuclear spallation occurs in radionuclides, e.g. <sup>235</sup>U, yielding 2–3 neutrons per fission event and releasing the energy of 100–200 MeV neutron<sup>-1</sup>. A photoneutron reaction is associated with the bremsstrahlung of fast electrons in a heavy target (e.g. tungsten); it yields one neutron per 20 electrons with the energy of 100 MeV and releases the energy of 2000 MeV neutron<sup>-1</sup>. Evaporation reaction in a heavy target gives rise to 40 cascade and evaporation (> 85%) neutrons per relativistic proton with the energy of 1000 MeV and releases the total energy of around 50 MeV neutron<sup>-1</sup>. Thus, the latter reaction has the advantage over the two others in that it produces more neutrons and ensures better cooling of the target.

Historically, however, the first intensive neutron sources were nuclear reactors in which continuous neutron fluxes were generated in course of spontaneous fission of uranium (steady state reactors). Up to now, these reactors remain major intensive neutron sources for physical research even though the proposal to use particle accelerators for this purpose dates back to the Fifties [29]. The first nuclear reactor was constructed under the supervision of E Fermi in Chicago, USA, in 1942. High-performance pulsed neutron sources based on electron accelerators appeared at Harwell, UK, in the 1950s [30].

There is no apparent advantage of reactors over accelerators in terms of neutron generation, but the span of 10 years and rapid progress in technology during that decade turned out to be critical for shaping the basic tendency in the further development of neutron research.

Since the early 1990s, the number of reactors have been progressively decreasing and is expected to be as small at the break of the next century as it was in the Sixties. Concurrently, accelerator technology has been on the rise during the last 30 years, and there are even greater prospects for its further advance in the near future. Therefore, it is safe to associate another breakthrough in the construction of intensive neutron sources with the development of accelerators, especially proton accelerators.

For all that, reactors remain important instruments of neutron research for several reasons. First, proton synchrotrons with the desired parameters are rather complicated and expensive machines. Second, practical realisation of highpowered target devices encounters many difficulties typical of such instruments, e.g cooling of the construction and ensuring its radiation resistance which depends on the fast neutron flux density in the target zone. Finally, there are still many active reactors in the world whose potentialities are far from being exhausted.

#### 2.1 Continuous flux sources

The majority of steady state reactors appeared between 1955 and 1960. Those were reactors of the first generation intended for target bombardment and radiation research. Following them after 1960 were reactors of the second generation designed to study radiation effects as well as to produce neutron beams. The first reactor of the third generation intended solely for neutron beam studies was commissioned at Brookhaven in 1965, i.e. 5 years later than the IBR pulse reactor at Dubna which had from the very beginning been used only for this purpose. Up to 1960, intensity of neutron beams and reactor power grew in parallel, but afterwards the former parameter rose more rapidly than the latter [31]. This difference has become especially pronounced since the early 1970s when reactors of the third generation came to be most extensively used in different countries: HFR (Institut Laue-Langevin, Grenoble, France), ORPHEE (Laboratoire Leon Brillouin, Saclay, France), IR-8 (Russian Research Centre 'Kurchatov Institute', Moscow, Russia), IBR-2 (JINR, Dubna, Russia), etc.

At present, there are around 50 research reactors in the world used in neutron beam studies. Most of them have been working for more than 30 years, that is for about their natural lifetime. Many reactors need to be modified or replaced by new ones.

In the end, the efficiency of a research reactor is determined by the performance of its experimental units. Table 1 lists steady state reactors of the third generation and some facilities of the second generation which are most effectively employed in beam research (a more comprehensive list of active research reactors is presented in Ref. [31].) The experimental devices are categorised into 5 types in compliance with the generally accepted classification, viz. diffract-ometers for elastic diffuse and elastic Bragg scattering, spectrometers for small-angle scattering, reflectometers, spectrometers for inelastic scattering, and other instruments. The

Country	City	Reactor	Operated since	Power, MW	Flux $\times 10^{14}$ , n cm <sup>-2</sup> s <sup>-1</sup>	Neutron channels	$\begin{array}{l} \text{Moderators} \\ (\text{C}-\text{cold}, \\ \text{H}-\text{hot}) \end{array}$	Neutron-scattering instruments *						
								D	SA	R	IE	0	Total	
Hungary	Budapest	WWR	1992	10	1	8	_	2	1	1	3	3	10	
Germany	Julich	FRJ-2	1962/72	23	2	8	С	4	3	1	7	3	18	
Germany	Berlin	BER-II	1973/91	10	1	9	С	6	1	1	5	1	14	
Denmark	Riso	DR-3	1960	10	1.5	4	С	1	1	0	5	0	7	
India	Bombay	Dhruva	1985	100	2	13	С	3	1	0	8	1	13	
Canada	Chalk River	NRU	1957	125	3	6	С	3	1	0	2	0	6	
The Netherlands	Petten	HFR	1961/70	45	1	12	_	3	1	0	2	1	7	
Russia	Gatchina	VVR-M	1959	16	1	14	_	3	2	0	1	6	12	
Russia	Moscow	IR-8	1981	8	1	12	С	2	0	0	3	5	10	
Russia	Ekaterinburg	IVV-2M	1966/83	15	2	6	_	4	1	0	1	0	6	
Russia	Gatchina	PIK	1998 (projected)	100	45	up to 50	2C, 2H	_	_	_	_	_	up to 50	
USA	Brookhaven	HFBR	1965	60	9	9	С	3	3	1	6	2	15	
USA	Oak-Ridge	HFIR	1966	100	30	4	_	4	1	0	5	0	10	
USA	Missouri	MURR	1966	10	1.2	6	_	3	2	1	2	6	14	
USA	Gettysburg	NBSR	1969	20	4	5	С	2	0	0	6	1	9	
France	Grenoble	HFR-ILL	1971/95	58	15	26	2C, 1H	11	2	0	10	2	25	
France	Saclay	ORPHEE	1980	14	2.5	20	2C, 1H	10	4	1	7	0	22	
Switzerland	Villigen	SINQ	1996	1	1	19	1C, 1H	3	1	2	3	3	12	
Sweden	Studswick	R-2	1960	50	4	8	С	6	0	0	2	0	8	
Japan	Ibaraki	JRR-3M	1990	20	2	26	С	4	1	0	10	5	20	

Table 1. High-flux neutron sources producing continuous beams and instruments for scattering experiments

\* D — diffractometers for elastic Bragg and elastic diffuse scattering, SA — spectrometers for small-angle scattering, R — reflectometers,

IE — spectrometers for inelastic scattering, O — other instruments

latter category comprises all instruments not included in the four other groups. Facilities for irradiation and activation analysis are beyond the scope of the present review.

It can be seen from Table 1 that the HRF and ORPHEE reactors are in all respects the most effective of the high-power and medium-power facilities respectively. The HRF reactor generates the highest neutron flux in terms of both absolute and specific (adjusted for power) intensity and provides the most developed infrastructure for experimental studies. The ORPHEE and IR-8 reactors appear to be the best ones among medium-power reactors.

Apart from technical characteristics, the cost of the reactor is of paramount importance, being largely dependent on its nominal power. Therefore, the average power to flux density ratio may serve as the arbitrary unit of the neutron production cost. The more experimental devices a reactor hosts the higher efficiency of its work and the cheaper production of one neutron. Table 1 shows that the HFR and ORPHEE reactors are superior to all the others in this respect.

On the whole, the number of up-to-date reactors in the world is insufficient to meet the requirements of physical research despite recently developed technical means for enhancing their efficiency, e.g. new moderators, beam-shaping neutron guides, and detectors. New reactors are currently under construction in many countries [31].

Prospects for further improvement of nuclear reactors with a view to obtaining higher extracted neutron fluxes are limited by technological reasons that largely turn on cooling problems [28]. In this sense, reactors of the HFR type and the PIK reactor (now under construction) appear to show the maximum capacity attainable in steady state facilities, ejecting thermal neutron fluxes of  $4-5 \times 10^{15}$  n cm<sup>-2</sup> s<sup>-1</sup>.

New sources based on proton accelerators (spallation sources) producing continuous neutron fluxes were proposed in the early Sixties to obtain higher fluxes. Proton beams may be either pulsed or continuous, but a pulse must always have the high-frequency microstructure which is immaterial for neutrons that passed the moderator. The Canadian ING project [32] was intended to obtain a flux of  $10^{16}$  n cm<sup>-2</sup> s<sup>-1</sup> from the moderator surface. However, it was discontinued in 1968 for the lack of an appropriate accelerator.

In 1987, the construction of a steady state spallation source was initiated in Switzerland following the decision to modify the isochronic cyclotron at the Paul–Scherer Institute, Villigen, with the purpose of having a proton flux of 1.5 mA with the energy of 600 MeV. The SINQ neutron source was projected by analogy with up-to-date reactors [33]. It is expected to start working in the end of 1996 and produce a neutron flux of  $10^{14}$  n cm<sup>-2</sup> s<sup>-1</sup>, similar to the majority of modern steady state reactors (see Table 1).

#### 2.2 Pulsed sources

The history of pulsed sources dates back to 1945 when a selfquenching pulse nuclear reactor (aperiodic pulse reactor) was constructed at Los Alamos in the framework of the Manhattan project [34]. Today, there are many reactors of this type throughout the world, but they are not normally used in physical research using ejected beams.

In 1955, an altogether new principle for periodic pulse reactors was suggested at the Physics and Energy Institute, Obninsk [35, 36]. The idea arose from the necessity to use beam choppers at steady state reactors to shape pulsed neutron beams for experiments in nuclear physics. Its realisation led to a further decrease in the efficiency of steady state reactors, low as it was.

The foundation of the IBR pulse reactor was laid at Dubna in 1957, within one year after JINR had been established. The work was headed by D I Blokhintsev and finished in 1960. That was the first reactor in which pulses were generated periodically at 5 and 50 Hz due to the partial rotation of the active zone [10, 37]. The average power of the reactor was only 1 kW, but the neutron flux was higher than in 10 MW steady state reactors combined with a chopper.

Successful work of the IBR reactor and its modified variants gave impetus to further progress in this field. In the mid-Sixties, a few more projects were initiated. First, the construction of the pulse SORA reactor with a movable reflector (average power 1 MW) was reported [38]. The reactor was to be built at the Euroatom Research Centre, Ispr, Italy. A high-power periodic pulse reactor (average power 30 MW) was projected at the Brookhaven National Laboratory, USA [39]. In 1964, the work on a new IBR-2 project was started at Dubna. This reactor was different from the first facilities of the IBR series in that its reactivity was modulated by a movable reflector and the active zone cooled with liquid sodium [34, 40]. Only the IBR-2 project has been realised of all others concerned with new high-flux pulse reactors, due to the previous experience with such systems at Dubna and Obninsk and the active participation of the former USSR Ministry of Mechanical Engineering (now the Russian Ministry of Atomic Energy).

The IBR-2 pulse reactor commissioned in 1984 produces the highest currently available thermal neutron flux amounting to  $10^{16}$  n cm<sup>-2</sup> s<sup>-1</sup>, in conjunction with the very high costefficiency: the lifetime of its active zone is around 20 years and that of the movable reflector is 7 years. Another characteristic feature of the IBR-2 reactor is the large neutron pulse duration (320 µs for thermal neutrons). This feature has until recently been regarded as a drawback. However, the development of the experimental technique on the IBR-2 reactor has demonstrated that modern instruments provide resolution comparable with that of the best pulsed sources for both elastic and inelastic scattering [41].

The first accelerator-based pulsed neutron source was constructed at Harwell in the early Fifties. A linear electron accelerator was used for the purpose. In 1959, a booster system (a combination of an accelerator and a breeding target) was suggested and realised in the same laboratory. The breeding target was a heavy-metal target in a subcritical assembly. Nuclear photoneutrons initiated a chain reaction in the assembly which caused a 10-30-fold rise in the neutron flux. The chain reaction in the subcritical assembly was possible only with the working accelerator which made the system distinct from a reactor.

Although electron accelerators are relatively easy to manufacture, they are not widely used today (barring nuclear physics) because of their low efficiency as compared with proton accelerators. The same refers to boosters. To our knowledge, Dubna is the only place where one booster still works and the construction of another is going ahead [41]. This is largely due to public protests against any system containing fission materials. However, the development of neutron sources appears to tend to a more extensive use of booster systems. At present, the Institute for Nuclear Research, Russian Academy of Sciences, projects such a system for the meson-factory in the town of Troitsk near Moscow, Russia [42]. In a sense, realisation of this tendency will depend on the practical results of the extensively discussed electronuclear technique for power production based on the use of booster systems.

Proton accelerators have been operated as pulsed neutron sources since early Seventies [3, 43]. ZING-P and ZING-P' prototypes were constructed at the Argonne National Laboratory, USA, in 1973 and 1975. The IPNS source has been working in the same laboratory since 1981. In 1971, similar facilities were commissioned at Los Alamos, and the high-power LANSCE source (recently renamed MLNSC) was installed there in 1985. The KENS source was commissioned at the National Laboratory of High Energies (KEK), Japan, in 1980. All these neutron sources of the second generation were based on accelerators for experiments in nuclear physics.

The first pulse spallation neutron source of the third generation (ISIS) on a specially designed accelerator started to work at the Rutherford–Appleton Laboratory, UK, in 1985. At present, ISIS is the most intensive, well-equipped, and convenient pulsed neutron source available [44, 45].

All these spallation neutron sources belong to the class of pulsed sources with the small duration of neutron pulses  $(\sim 10 \ \mu s)$  or Short Pulsed Sources (SPS). Of late, much attention has been focused on the development of sources with the pulse duration of the order of hundreds of microseconds (LPS). This can be accounted for by the high construction costs of proton accumulators with energies of several GeV necessary to produce higher neutron fluxes. It is much cheaper to build up a high-power linear proton accelerator. In this case, however, the neutron pulse duration increases. Experience with the first LPS (IBR-2) indicates that it is in no way inferior to SPS. This experience can be used in constructing LPS on proton accelerators. Such a source is expected to be commissioned in coupling with the linear accelerator at Moscow meson-factory in 1996 [42]. Another project of a high-power LPS is currently elaborated at Los Alamos.

Table 2 lists intensive pulsed neutron sources used to study condensed matter. All the laboratories listed in the table have projects for increasing the capacity of their reactors and obtaining higher neutron fluxes. Moreover, there are new projects among which AUSTRON, JHP, and ESS are the most advanced ones. AUSTRON is an ISIStype reactor for Middle Europe, JHP is the Japanese hadron project for a high-power proton accelerator with the energy of 1 GeV and average power at the target 1 MW, ESS is the project for the European spallation source of the next generation with the average power 5 MW, i.e. 30 times that of the ISIS [46].

### 2.3 Comparison of different sources

When comparing different types of sources, many factors need to be taken into consideration [3]. Each type has its merits and demerits, and only the comparison of experimental findings may reveal advantages and disadvantages of one or another source. Moreover, comparing diffraction data precision and collection rate for one and the same sample in a standard polycrystal structural study yields but qualitative conclusion since  $d_{hkl}$  (h, k, l are the Miller indices) for the position and thermal atomic parameters are different because of the difference in the observed interplanar distance ranges and the behaviour of resolution function R(d) (see, for instance, Ref. [47] where the authors compare data for Al<sub>2</sub>O<sub>3</sub>). It is known from practical experience that measurements using time-of-flight and double-axis diffractometers of the same class (i.e. with the approximately similar resolving capacity and full fluxes at the sample) bring about qualitatively identical structural information even though some details may differ considerably.

Therefore, in cases where only one measurement is needed at a given wavelength (e.g. measurement of a Bragg or phonon peak), spectrometers with crystalline monochromators on a continuous flux source may prove especially efficacious. When measurements are made in a wide neutron

Country, location	Source, operated since	Target power, kW	Beam energy, MW	Flux $\times 10^{14}$ , n cm <sup>-2</sup> s <sup>-1</sup>		Pulse length,	Frequency pulse,	Neutron channels	Cold modera-	Neutron-scattering instruments *					
				pulsed	average	μs	s <sup>-1</sup>		tors	D	SA	R	IE	0	Total
Short Pulse Se	ources (SPS)														
UK															
Chilton	ISIS, 1985	160	800	10	$7 \times 10^{-3}$	20 - 30	50	14	2	5	2	2	6	1	16
USA															
Argonne	IPNS, 1981	7	450	3	$2 \times 10^{-3}$	20 - 30	30	12	1	5	1	2	3	0	11
Los Alamos	MLNSC, 1985	50	800	7	$5  imes 10^{-3}$	20 - 30	20	16	_	3	1	1	2	_	7
Japan															
Tsukuba	KENS, 1980	3.5	500	1	$7  imes 10^{-4}$	30-35	15	15	1	4	2	_	7	2	15
Long Pulse So	ources (LPS)														
Russia															
Dubna	IBR-2, 1984	2000	2000	100	$8 \times 10^{-2}$	320	5	14	1	5	1	2	3	1	12
Troitsk	IN-0.6, 1996 (projected)	30	600	3.5	$9 \times 10^{-3}$	50	50	4	-	1	_	_	1	_	2

Table 2. Pulse neutron sources and instruments for scattering experiments

\* D — diffractometers for elastic Bragg and elastic diffuse scattering, SA — spectrometers for small-angle scattering, R — reflectometers, IE — spectrometers for inelastic scattering, O — other instruments

TE — spectrometers for melastic scattering, O — other mistruments

wavelength range or fixed scattering geometry is required, the time-of-flight method should be preferred.

In scattering experiments, a major characteristic of a source is the average neutron flux which does not only dictate the design of the study but also determines the possibility to enhance the accuracy of measurements, to study small or complex objects and objects with small scattering crosssections, and to analyse neutron polarisation before and after scattering. Comparison of Tables 1 and 2 in terms of this characteristic demonstrates the advantage of steady state reactors over pulsed neutron sources.

However, analysis of experimental conditions in scattering studies with pulsed and continuous beam sources [48] has shown that, for ideal instruments requiring neutron monochromatisation, the time-averaged flux in a pulsed source is equivalent to the peak flux. This means that in such cases conditions for experimentation on the existing pulsed sources may be better than those where a steady state reactor is used.

Important characteristics of pulsed sources are the repetition frequency and the duration of neutron pulses. The higher the repetition rate the higher the average flux. On the other hand, the repetition frequency must not be too high and lead to 'the overlap' of timed neutrons from neighbouring pulses. The optimum pulse frequency depends on the pulse duration and the type of the experiment. The longer the pulse and the farther the instrument from the source the lower the repetition rate must be. In sources with the high repetition rate, it sometimes needs to be artificially lowered using special choppers. For example, one has to cut off four pulses of the five when using a High-Resolution Power Diffractometer (HRPD) at the ISIS source with the 100 m flight path and the frequency of 50 s<sup>-1</sup> in the range between 0.5 and 2.5 A.

A neutron pulse in all sources is formed by moderators, and its shape is a convolution of fast neutron pulses generated in the active zone and the response function of the moderator. Fast neutron pulses in spallation sources are so short (ca. 0.1 µs) that their length does not affect the final result which largely depends on the characteristics of the moderator optimised in terms of either neutron yield or pulse length [49]. In case of thermal neutrons (E < 0.5 eV) used in condensed matter physics, the pulse duration is  $\Delta t_0 > 10$  µs. In a pulse reactor, fast neutron pulses are long (ca.  $200 \ \mu$ s) and grow even further with moderation, i.e. such reactors are LPS.

Neutron scattering experiments measure the doubledifferential scattering cross-section per the solid-angle element  $d\Omega$ :

$$\frac{\mathrm{d}^2 \sigma}{\mathrm{d}\omega \,\mathrm{d}\Omega} = \frac{k_2}{k_1} \, S(\mathbf{Q}, \omega) \,, \tag{1}$$

where  $\mathbf{k}_1$ ,  $\mathbf{k}_2$  are the wave vectors of incident and scattered neutrons respectively,  $\mathbf{Q} = \mathbf{k}_1 - \mathbf{k}_2$  is the scattering vector, and

$$h\omega = \frac{h^2}{2m}(k_1^2 - k_2^2)$$

is the transferred energy. The wave vector is related to the neutron wavelength by the expression  $|\mathbf{k}| = k = 2\pi/\lambda$ . One of the parameters measured in experiments with pulsed neutron sources is the neutron's time-of-flight *t* across the sum of distances from the source to the sample  $L_1$  and from the sample to the detector  $L_2$ . In order to pass from *t* to the wavelength, the following equation is used:

$$\lambda = \frac{h}{mv} \approx \frac{4t}{L_1 + L_2} , \qquad (2)$$

where v is the neutron velocity in m s<sup>-1</sup>,  $\lambda$  is measured in A, t in ms, and L in m. All information about the properties of the sample is contained in the scattering function  $S(\mathbf{Q}, \omega)$ .

The accuracy of measurements (instrumental resolution) in elastic neutron scattering experiments depends on the accuracy of measuring momentum transfer which is in turn dependent on the pulse duration of a given source  $\Delta t_0$  and geometric uncertainties of the scattering process. In experiments on small scattering and reflectometry the neutron pulse duration is unessential due to a large geometric contribution [3] while in diffraction studies the two contributions are almost identical. Special methodology is needed to improve the instrumental resolution in LPS studies. Its value has been demonstrated by the comparative analysis of the measurements of the same samples in experiments with the IBR-2 and ISIS sources, including those on inelastic neutron scattering [41]. The use of these methods entails the inevitable loss of intensity, but higher average neutron fluxes from IBR-2 ensure almost equal data collection rate.

Thus, the higher the intensity of the source the more possibilities for its use in scattering experiments.

### 3. Some aspects of time-of-flight diffractometry

### 3.1 Time-of-flight diffractometers

The universal scheme of a standard time-of-flight diffractometer is presented in Fig. 1. Following the slowdown to thermal energies, neutrons from a pulsed source traverse the primary path undergoing collimation and monochromatisation, then scatter at the sample, and are eventually recorded at a fixed angle by the detector. The analyzer writes the spectrum unfolded over the neutrons' time-of-flight from the moderator to the detector into the on-line memory. Spectra of sequential pulses of the source are summed up to accumulate necessary statistics. Synchronisation of the analyzer and the power pulses of a neutron source is performed using special starting pulses. Vectors  $\mathbf{k}_1$  and  $\mathbf{k}_2$  indicate directions of primary and scattered neutron beams, and their absolute values vary continuously with the time-of-flight. Instruments of this type are currently referred to as conventional time-offlight diffractometer to distinguish them from the recentlydeveloped Fourier diffractometers in which the time-of-flight principle is likewise employed to unfold spectra. Furthermore, we shall compare the efficiency of time-of-flight diffractometers (conventional and of the Fourier-type) with that of double-axis diffractometers [1-4] on steady state reactors using monochromatic neutron beams.



**Figure 1.** The functional scheme of time-of-flight diffractometer: A — pulsed source, B — moderator, C — primary flight path, D — sample, E — detector, F — analyzer, G — working memory.  $\mathbf{k}_1$  and  $\mathbf{k}_2$  are the wave vectors of incident and scattered neutrons respectively.

First diffractometers for the analysis of polycrystal substances [9, 11] were based on the scheme shown in Fig. 1. This scheme has not undergone substantial changes since that time.

Modern time-of-flight diffractometers for polycrystal studies have several large-area detectors and relatively long flight path between the moderator and the sample  $L_1$ , to ensure high time-of-flight resolution which is always  $\sim 1/L_1$ . The moderator is followed by the chopper (filter) which

eliminates background source neutrons from the beam including those from one or more main pulses, whenever their frequency needs to be reduced. A basic element for the formation of thermal neutron beams is the curved neutronguide tube. It allows the loss of intensity to be significantly diminished by virtue of the large flight path; moreover, it serves as an additional filter eliminating fast neutrons from the beam and  $\gamma$ -rays from the source. The main highresolution power detector is in a fixed position corresponding to the maximally feasible scattering angle. Additional detectors may also be at fixed scattering angles and arranged on a platform rotating around the central axis of the diffractometer. The massive central table supports furnaces, cryostats, and other devices hosting a sample.

At present, the majority of working time-of-flight diffractometers are used in experiments on polycrystals. The DN-2 diffractometer at the IBR-2 reactor [50] has the highest neutron flux at the sample (up to  $2 \times 10^7$  n cm<sup>-2</sup> s<sup>-1</sup>) while HRPD at the ISIS provides the best resolution (up to  $5 \times 10^{-4}$ ) [51].

Experiments on single crystals using time-of-flight diffractometers are organised in a similar way. The first onedetector diffractometer to be used in single crystal studies was constructed as early as 1964 [52]. But even at that time, it was clear that such studies must be carried out with multi-counter systems or position-sensitive detectors because this allows to probe a plane or a volume in the reciprocal space (Fig. 2).



**Figure 2.** Reciprocal space region observed with a time-of-flight diffractometer (one-dimensional PSD).  $(a^*, b^*)$  is the reciprocal lattice crosssection,  $\mathbf{k}'_1$  is the primary beam direction,  $\mathbf{k}'_2$  is the average direction of a scattered beam. Recording is performed in the scattering angle range from  $2\theta_{\min}$  to  $2\theta_{\max}$  and in the neutron wave vector range from  $\mathbf{k}'_{\min}$  to  $\mathbf{k}'_{\max}$ . Points are lattice sites within the observed region. Primes at the wave vectors indicate that their values are divided by  $2\pi$ .

One-dimensional (linear) Position-Sensitive Detectors (PSDs) were reported to be used in Russia [53] and Japan [54] in the early Eighties. The use of PSDs in conjunction with the wavelength scanning of the diffraction spectrum promoted a radical change in the design of experiments and the realisation of the so-called 'multidimensional diffractometry'. Indeed, multidimensionality is reduced to a two- or three-dimensional case when one- or two-dimensional PSDs respectively are used. In either case, one coordinate is always time-og-flight, and time-scanning corresponds to scanning

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reciprocal crystal space along the radius-vector  $\mathbf{H}$ . Other coordinates are the detector position groups; in a reciprocal space, this corresponds to the scanning in the plane perpendicular to  $\mathbf{H}$ .

Nowadays, there are some ten conventional time-of-flight diffractometers in the world intended for single crystal experiments. Structural single crystal studies require neutron fluxes of around  $10^6$  n cm<sup>-2</sup> s<sup>-1</sup> and mean resolution  $10^{-2}$ . Up-to-date PSDs with good spatial resolution are crucial for the quality of diffraction experiments.

In the early 1980s, one more line in the development of time-of-flight diffractometers emerged: neutron diffractometry in conjunction with correlation analysis. The scheme of these studies includes a special pseudo-random or Fourier chopper after the moderator (B in Fig. 1) and the use of statistical analysis for interpreting experimental diffraction spectra. These two new elements make the standard scheme much more complicated and should be considered in greater detail (see the next section). We are aware of two currently operated Fourier diffractometers on steady state reactors [23, 24] and one on the IBR-2 pulsed source [25]. They meet all the requirements for present-day powder neutron diffraction due to very high flux intensity (up to  $10^7$  n cm<sup>-2</sup> s<sup>-1</sup>) and resolution (down to  $5 \times 10^{-4}$ ).

The use of continuous spectra and the time-of-flight technique for the wavelength scanning of the diffraction picture has obvious advantages. The most important one is a manyfold increase in the efficiency of using neutrons from the source. This accounts for a comparable or (in certain special experiments) even much higher diffraction data collection rate than is feasible with a time-of-flight diffractometer, notwithstanding far lower intensity of time-averaged neutron fluxes provided by modern pulsed sources as compared with that available using steady state reactors.

Modern time-of-flight diffractometers work in a wide wavelength range of 0.9-8 A even though either very short (less than 0.5 A) or very big (up to 20 A) wavelengths are normally used. This allows a wide range of *d*-spacings to be covered by a small number of detectors. In fact, only two detectors positioned at scattering angles 20° and 60° are needed to observe the interval  $d_{hkl}$  between 0.46 and 23 A when working in the 0.9 A  $\leq \lambda \leq 8$  A range [in accordance with the Bragg equation  $d = \lambda/(2 \sin \theta)$ ].

Two- or three-dimensional diffractometry of the reciprocal space is easy to perform using a time-of-flight diffractometer. The time-of-flight technique provides the scanning of the radius-vector of a reciprocal lattice while the position groups of one or two-dimensional position-sensitive detectors allow for transverse scanning.

The resolution  $\Delta d/d$  of a time-of-flight diffractometer for polycrystals is easy to bring to 0.003 and even to 0.0005 (in special cases), it being virtually independent of  $d_{hkl}$ .

Other traditionally valued advantages are the possibility to make measurements in fixed geometry (which is of importance for working with high-pressure chambers) and pulsed neutron bombardment of a sample. The latter technique allows external impacts on the sample to be realised in the pulsed regime which leads to a marked increase in the amplitude of these effects.

A serious drawback of time-of-flight diffractometers is normally low data precision as compared with that available with a double-axis diffractometer. This can be accounted for by the necessity to introduce a large number of wavelengthdependent corrections when converting measured diffraction peaks to structure factors. The most important of these corrections is the effective spectrum of neutrons incident on the sample including transmission on flight paths and detector efficiency. This correction is largely responsible for the accuracy of experimentally measured structure factors for crystals although it may vary tenfold depending on the wavelength and the methods for its determination need to be considerably improved.

### 3.2 Definition of structure factors

The structure factor  $F_{\rm H}$  [1, 2] related to the reflection intensity (diffraction peak intensity) *I* measured in a diffraction experiment is a basic experimentally measured parameter used in the structural analysis. Similar to the case of X-ray diffraction, *I* may be represented in the kinematic approximation as a product of the incident flux  $\Phi$ , the squared modulus of the crystal structure factor  $|F|^2$ , and a certain function  $Q_{\rm L}$ (sometimes called the Lorentz factor) which takes into account geometrical and correction factors:

$$I = \Phi |F|^2 Q_{\rm L} \,. \tag{3}$$

The general form of the structure factor is identical for different types of radiation:

$$F_{\mathbf{H}} = \sum_{j}^{N} b_j \exp(2\pi i \, \mathbf{H} \mathbf{R}_j) \exp(-W_j) \,, \tag{4}$$

where **H** is the vector of the reciprocal lattice of the crystal,  $\mathbf{R}_j$  is the radius-vector of the *j*-th atom in the elementary crystal cell,  $\exp(-W_j)$  is the Debye–Waller factor taking into account thermal oscillations of the *j*-th atom; the sum is taken over all the atoms of the elementary cell. The dependence of the structure factor on the type of radiation is determined by quantities  $b_j$ , that is atomic form-factors for X-rays and coherent scattering lengths (taking into account both nuclear and magnetic neutron scattering) in the case of neutron diffraction. Distinct nature of  $b_j$  quantities is responsible for major differences between neutron and X-ray structural analyses.

Determination of coordinates of light atoms, especially those of hydrogen, has been extensively used from the very beginning of neutronographic studies. Also, the isotope contrasting technique has recently come to be widely employed as an experimental tool.

Similar to the situation in X-ray structural analysis, the neutron structure factor is related by the Fourier transformation to the scattering density, i.e. the distribution density for the coherent scattering length in an elementary cell:

$$b(\mathbf{R}) = \sum_{hkl} F(\mathbf{H}_{hkl}) \exp(-2\pi \mathrm{i} \, \mathbf{H}_{hkl} \mathbf{R}) \,, \tag{5}$$

where  $\mathbf{H}_{hkl}$  stands for a discrete set of vectors of the crystal reciprocal lattice and  $\mathbf{R}$  is any vector in the elementary cell. The construction of scattering density maps is the most general purpose of the crystal structural analysis which can be achieved in neutron diffraction using a standard approach, in accordance with Eqn (5). A specific feature of this step is the absence of the positive definiteness  $b(\mathbf{R})$  which is present in the X-ray diffraction analysis. Sometimes, this hinders the analysis but, on the other hand, it is this feature that allows the nuclear density distribution of hydrogen atoms in a cell to be examined in detail whereas the coherent hydrogen scattering length is negative and in sharp contrast with the distribution density of other atoms.

In neutron diffraction, a structure factor is traditionally related to the coherent cross-section of neutron scattering by a single crystal volume obtained from Eqn (1) in case of elastic scattering [1, 2]:

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \sigma(\mathbf{Q}) = \frac{(2\pi)^3}{V_c^2} \left| F(\mathbf{H}_{hkl}) \right|^2 \varphi(\mathbf{Q} - 2\pi \,\mathbf{H}_{hkl}) \,, \tag{6}$$

where  $V_c$  is the volume of an elementary cell while  $\varphi$  defines the shape and the size of sites in the reciprocal lattice. Function  $\varphi$  depends, in particular, on the size and orientation of the mosaic blocks in a crystal, dispersion of interplanar distances, etc. In the case of an ideal crystal,  $\varphi$  may be regarded as the  $\delta$ -function.

The coherent scattering cross-section is in turn related to the experimentally measured intensity of the diffraction peak *I* which is in the general case, the three-dimensional function of a transmitted pulse, a convolution-like integral

$$I(\mathbf{Q}_0) = \int R(\mathbf{Q} - \mathbf{Q}_0)\sigma(\mathbf{Q}) \,\mathrm{d}\mathbf{Q}\,,\tag{7}$$

where *R* is the three-dimensional resolution function of the diffractometer and  $\mathbf{Q}_0$  is understood to be the transmitted neutron pulse to be detected by the diffractometer.  $|F(\mathbf{H}_{hkl})|^2$  is normally obtained by integrating  $I(\mathbf{Q}_0)$  over all  $\mathbf{Q}_0$  which contribute to peak intensity. This procedure eliminates the resolution function which is frequently unknown, because

$$\int I(\mathbf{Q}_0) \, \mathrm{d}\mathbf{Q}_0 = \iint R(\mathbf{Q} - \mathbf{Q}_0)\sigma(\mathbf{Q}) \, \mathrm{d}\mathbf{Q} \, \mathrm{d}\mathbf{Q}_0$$
$$= \int \sigma(\mathbf{Q}) \, \mathrm{d}\mathbf{Q} = \text{const} \,. \tag{8}$$

The constant in Eqn (8) depends on the reciprocal space scanning conditions; for a time-of-flight diffractometer (fixed crystal, wavelength scanning), the relationship between integrated intensity of the diffraction peak and its structure factor may be written as

$$I_{\text{int}} = \int I(\mathbf{Q}_0) \, \mathrm{d}\mathbf{Q}_0 \sim \Phi(\lambda_0) Q_{\text{L}} \left| F(\mathbf{H}_{hkl}) \right|^2 A(\lambda_0, \theta_0) y(\lambda_0, \theta_0),$$
(9)

where  $\lambda_0$  and  $\theta_0$  are the neutron wavelength and scattering angle respectively at which the diffraction peak with Miller indices (h, k, l) is observed,  $\Phi(\lambda_0)$  is the spectral density of the neutron flux at the sample, A is the absorption factor, y is the extinction coefficient, and  $Q_{\rm L} = \lambda_0^4/(2\sin^2\theta_0)$  is the Lorentz factor. Therefore, by measuring  $I(\mathbf{Q}_0)$  and calculating or measuring  $\Phi(\lambda_0)$ ,  $A(\lambda_0, \theta_0)$ , and  $y(\lambda_0, \theta_0)$ , it is possible to find  $|F(\mathbf{H}_{hkl})|^2$  using Eqn (9) which is the extended representation of Eqn (3). Furthermore, by determining phases (or signs, for a centrosymmetric structure) of structural factors, one can specify atomic coordinates and thermal factors of the structure by the least squares method or construct the scattering density distribution using Eqn (5).

Another usual problem of the crystal structural analysis is the examination of the site shape in the reciprocal lattice, i.e.  $\sigma(\mathbf{Q})$  measurements. It is desirable to have as narrow resolution function as possible (a  $\delta$ -like one in the limit) in order to satisfy the condition  $I(\mathbf{Q}) \sim \sigma(\mathbf{Q})$ . For measuring  $\sigma(\mathbf{Q})$ , it is necessary to vary the argument of the  $\varphi$ -function, i.e. to scan the reciprocal space. Scanning with a time-of-flight diffractometer is possible by varying the neutron wavelength and the directions of vectors  $\mathbf{k}_2$  and  $\mathbf{H}$ . For instance, if a two-dimensional PSD is used to detect scattered neutrons, scanning with respect to the wavelength and the direction  $\mathbf{k}_2$  is performed automatically. The choice of a specific region of the reciprocal space for scanning is realised by the appropriate orientation of the crystal (direction of vector  $\mathbf{H}$  relative to  $\mathbf{k}_1$ ).

Let us turn now to the structural analysis of a polycrystal substance as a variant of the analysis of formula (7). In this case, the scattering cross-section (6) must be averaged over orientations of the vector **H** which allows the measured diffraction spectrum to be written as a parametric function at the interplanar distance scale d (d = 1/H):

$$I(d) \sim \Phi(d)A(d) \sum_{hkl} j_{hkl} |F(\mathbf{H}_{hkl})|^2 Q_{\mathsf{L}} \varphi(d_{hkl} - d), \quad (10)$$

where A and  $Q_L$  are the absorption and Lorentz factors as before, (hkl) is the triple of the Miller indices, and j is the multiplicity factor. Parameters of function (10) include atomic coordinates and thermal factors, occupation factors for crystallographic positions, and parameters of an elementary crystal cell. Specification of these quantities is feasible by the least square method. Also, function (10) allows the extinction and texture of the sample to be taken into consideration. A major difference of Eqns (9) and (10) from the respective formulas for monochromatic radiation (when scanning is with respect to the scattering angle) consists in the appearance of neutron wavelength dependences of functions  $\Phi$ , A, and y. The correct consideration of these dependences is of paramount importance in precise structural experiments. Let us consider them at greater length.

## **3.3 Introduction of corrections in the calculation of structure factors**

**3.3.1 Determination of the effective neutron spectrum.** The function  $\Phi$  in Eqns (3), (9), and (10) stands for the effective neutron spectrum  $\Phi_{\text{eff}}$ , that is spectral flux density in the primary beam with regard for the neutron transmission on flight paths before and after scattering  $\eta$  and the detector efficiency  $\mu$ :

$$\Phi_{\rm eff}(\lambda) = \Phi(\lambda)\eta(\lambda)\mu(\lambda)$$
.

 $\Phi_{\rm eff}$  being determined in standard geometry for diffraction experiments and with the same detector, independent measurements of  $\Phi$ ,  $\eta$ , and  $\mu$  are no longer needed. The most common technique for measuring  $\Phi_{\rm eff}$  implies the use of an incoherent scatterer, most often vanadium whose differential elastic incoherent scattering cross-section  $\sigma_{inc}$  is assumed to be isotropic and independent of the neutron wavelength. However, weak dependences of  $\sigma_{inc}$  on both the scattering angle and  $\lambda$  do actually exist and, in principle, must be taken into account. For this purpose, a special procedure has been developed [55] which introduces the  $\lambda$ - and  $\theta$ -dependent correction factor  $\xi$ . At  $L_1 \gg L_2$  ( $L_1$  and  $L_2$  are neutron paths before and after scattering) which is usually fulfilled, this correction in a wide waverange does not exceed 10%. At the same time the case of small  $\lambda$  and large  $\theta$  requires special consideration.

Scattering from vanadium may be actually employed for the calibration up to the wavelength of 8 A; further on, the effect to background ratio becomes too small. To expand this limit, one may use diffraction at a polycrystal showing diffraction peaks in the long-wave range and to measure the spectrum at  $\lambda > 12$  A based on the neutron reflection from a mirror. A polycrystal of Fe(CN)<sub>6</sub>K<sub>3</sub> and a nickel mirror were used for this purpose in a study carried out on the DN-2 diffractometer at Dubna. Simultaneous measurement of scattering spectra at vanadium, the mirror, and the polycrystal allowed the entire required waverange from 0.7 to 22 A to be covered [55].

**3.3.2** Absorption and extinction corrections. The initial expressions for these corrections do not differ from those for the case of double-axis diffractometer. For the absorption factor, there is the integral over the sample volume

$$A(\lambda,\theta) = \frac{1}{V} \int \exp(-\mu x) \,\mathrm{d}V, \qquad (11)$$

where  $\mu = \mu(\lambda)$  is the linear attenuation coefficient dependent on the neutron wavelength and x is the neutron path in the sample. For all elements excepting hydrogen and some isotopes with the strong absorbtion (<sup>113</sup>Cd, <sup>149</sup>Sm, <sup>155</sup>Gd, ...), the wavelength dependence is exhibited only by the absorption cross-section

$$\mu(\lambda) = \sum_{i} n_i \left( \sigma_{\rm inc} + \sigma_{\rm abs} \, \frac{\lambda}{\lambda_0} \right)_i, \tag{12}$$

where  $n_i$  is the number of type *i* atoms in a unit volume,  $\sigma_{inc}$  and  $\sigma_{abs}$  are the cross-sections of incoherent scattering and absorption respectively, the sum is taken over all the atoms in an elementary cell,  $\lambda_0$  is the wavelength at which the absorption cross-section value is taken. The incoherent elastic neutron scattering cross-section for hydrogen  $\sigma_{H,inc}$  is known to vary from 20 to 80 b depending on the strength of hydrogen bonds in the structure and the energy of an oncoming neutron. The following approximation for it was suggested in Ref. [56]:

$$\sigma_{\rm H,\,inc} \approx 35.2 + 12(\lambda - 1) \,\mathrm{b}\,,$$
(13)

where  $\lambda$  is taken in A. This dependence is fairly well fulfilled in the wave range of 0.7–3.0 A for organic compounds and hydrates. In other situations, an empiric absorption correction is needed for hydrogen-containing samples.

For the aforementioned isotopes having strong resonance in the energy thermal region, not only absorption but also the coherent scattering length shows strong (resonance-like) wavelength-dependence [57] which ought to be taken into consideration.

The analysis reported in Ref. [58] has demonstrated that the extinction correction of intensities measured on a time-offlight diffractometer does not require reformulation of the Zachariasen, Cooper-Rose, and Becker-Copens algorithms widely used when measurements are performed with a double-axis diffractometer. Doubtless, it is possible to use the most up-to-date algorithm developed in Ref. [59] which removes some inaccuracies of the Bekker-Copens method.

The simplest of the above algorithms showing marked wavelength dependence of the extinction coefficient is the Zachariasen algorithm [60] which leads, in the case of secondary extinction only, to the expression

$$y(\lambda,\theta) = \left[1 + \frac{2rQ_0T}{\lambda}\sqrt{1 + \left(\frac{r}{\lambda g}\right)^2}\right]^{-1/2},$$
 (14)

where  $Q_0 = \lambda^3 F^2 / (V_c^2 \sin 2\theta)$ , *T* is the mean neutron path in the sample, *r* and *g* are the parameters corresponding to the radius of the crystal's mosaic blocks and the degree of their disorientation respectively  $[g = 1/(2\sqrt{\pi\eta})$ , where  $\eta$  is mosaic spread of the sample]. In the case of two limiting crystal types: I (when  $r \ge g\lambda$ ) and II (when  $r \le g\lambda$ ), it is possible to obtain the following expression for  $y(\lambda, \theta)$ :

(I) 
$$y(\lambda, \theta) = (1 + 2gQ_0T)^{-1/2}$$
,  
(II)  $y(\lambda, \theta) = \left(1 + \frac{2rQ_0T}{\lambda}\right)^{-1/2}$ . (15)

Evidently, the extinction coefficient always drops rapidly with increasing wavelength.

Typically, the most marked wavelength dependence of functions  $\Phi$ , A, and y is shown by the effective neutron spectrum that may experience a 100-fold and greater variation in the working waverange. It is worthwhile to note, however, that wavelength-related smooth changes of these quantities are responsible for the weak influence of the probable incorrectness of taking them into account at the transition from intensities to structure factors on the crystal atomic coordinates being determined, even though the thermal parameter values of the atoms may be grossly distorted.

### 3.4 Resolution of time-of-flight diffractometers

The resolution is a most important characteristic of a diffractometer which largely determines the possibility to solve diffraction-related problems. This accounts for its special consideration in the present review. In the general case, resolution is the three-dimensional function  $R(\mathbf{Q})$  which depends in a very complicated manner on the transmitted pulse. In principle, it can be calculated if individual probability distributions affecting the shape of the diffraction peak are known. In most cases, R may be written only in the form of multiple integrals which can not be calculated analytically: the only way is to measure independent distributions and perform numerical calculations. Sometimes, simplifications are possible which allow to obtain expressions for practically important cases of two and one-dimensional profiles of diffraction peaks. Let us briefly consider these cases, taking into account the crystal mosaic which has great effect on the shape of diffraction peaks even if it is not involved in the resolution function proper.

The simplified scheme of a diffraction experiment is presented in Fig. 3. When scattering angles are not very

 $2\theta_c$ 

 $k_{10}$ 

М



large  $(\tan \theta_0 \ll 2/\phi^2)$ , where  $\phi$  is the vertical divergence of a neutron beam), it is sufficient to consider the projection of neutron paths upon the horizontal surface and take into account the distributions:  $P(\gamma_1)$  is the probability density for neutron incidence on the sample at an angle  $\gamma_1$  to the direction  $\mathbf{k}_{10}$ ,  $W(\gamma_2)$  is the density of the number of the mosaic blocks oriented at an angle  $\gamma_2$  to the average direction  $\mathbf{H}_0$ , and  $Z(\varepsilon)$  is the shape of a neutron pulse outgoing from the moderator. Vectors  $\mathbf{k}_{10}$  and  $\mathbf{k}_{20}$  in Fig. 3 denote average directions from the source to the sample and from the sample to the detector. The variables  $\gamma_1$  and  $\gamma_2$  are interrelated through expressions

$$k\sin\theta = \pi H$$
,  $\mathbf{k}_2 - \mathbf{k}_1 = 2\pi \mathbf{H}$ ,  $k_1 = k_2$ . (16)

The probability density for the registration by the detector of a neutron with the wave vector  $\mathbf{k}_2$  is  $G_s \sim P(\gamma_1) W(\gamma_2)$ ; it follows from Eqn (16), with regard for the smallness of angles  $\gamma_1$  and  $\gamma_2$ , that

$$\gamma_1 + \gamma = 2\gamma_2, \quad \gamma_1 - \gamma = 2\xi \tan \theta_0, \quad (17)$$

where  $\gamma$  is the angle between vectors  $\mathbf{k}_{20}$  and  $\mathbf{k}_2$ ,  $\xi = (k - k_0)/k_0$  is the relative deviation of the modulus **k** from its average value  $k_0 = k_{10} = k_{20}$ . Solution of the system (17) with respect to  $\gamma_1$  and  $\gamma_2$  yields for  $G_s$ :

$$G_{\rm s}(\gamma,\xi) \sim P(\gamma + 2\xi \tan \theta_0) W(\gamma + \xi \tan \theta_0) \,. \tag{18}$$

Taking into account contributions to Eqn (18) of random variables that do not correlate with  $\xi$  and  $\gamma$  is accomplished by the calculation of the corresponding convolutions. For example,  $Z(\varepsilon)$  is taken into account by the transition from  $G_s$  to

$$G'_{\rm s}(\gamma,\xi) \sim \int G_{\rm s}(\gamma,\xi-\varepsilon)Z(\varepsilon)\,\mathrm{d}\varepsilon\,.$$
 (19)

Function  $G'_{s}(\gamma, \xi)$  describes the shape of two-dimensional diffraction peaks and coincides, for a single crystal with a small mosaic spread, with the projection of the diffractometer resolution function  $R(\mathbf{Q})$  upon the scattering plane.

For the purpose of estimation, it is normally sufficient to use the approximation by Gaussians with the appropriate dispersions instead of exactly setting the probability density for individual distributions. In this case, the two-dimensional distribution  $G'_s(\gamma, \xi)$  looks like an ellipse rotated in a certain way relative to the coordinate axes  $\gamma$  and  $\xi$ . It is therefore easy to obtain dispersion in variables  $\gamma$  and  $\xi$  for both the overall distribution  $G'_s(\gamma, \xi)$  and its projections upon axes  $\gamma$  and  $\xi$ :

$$D_{\gamma} = \gamma_0^2 + 4\eta^2$$
,  $D_{\xi} = D_t + \frac{\gamma_0^2 + \eta^2}{\tan \theta_0}$ , (20)

where  $\gamma_0^2$ ,  $\eta^2$ , and  $D_t$  are distribution dispersions  $P(\gamma_1)$ ,  $W(\gamma_2)$ , and  $Z(\varepsilon)$  respectively.

The resolution function becomes one-dimensional in the analysis of polycrystal matter and is normally expressed in the form  $R(d) = \Delta d/d$ , where  $\Delta d$  is the full width at the half-maximum distribution for the interplanar distance:

$$R(d) = \frac{\Delta d}{d} = \left(R_t^2 + R_\theta^2\right)^{1/2} = \left[\left(\frac{\Delta t_0}{t}\right)^2 + \left(\frac{\Delta \theta_0}{\tan \theta_0}\right)^2\right]^{1/2},$$
(21)

where  $R_t = \Delta t_0/t$  serves to denote the time-of-flight-dependent part of R(d),  $\Delta t_0$  is the pulse width of neutrons from the source, t is the time of their flight along the entire path L from the moderator to the detector, and the geometric term  $R_{\theta} = \Delta \theta_0 / \tan \theta_0$  contains all angular uncertainties of the scattering process associated with the divergence of the primary neutron beam, sample size, scattered beam collimation, etc. Figure 4 shows the typical form of R(d) for a diffractometer in terms of time-of-flight for cases when  $\Delta t_0$ is t-independent (HRFD at the IBR-2 reactor, Dubna) or is strictly proportional to t (the HRPD at the ISIS source).



**Figure 4.** The calculated resolution function  $R(d) = \Delta d/d$  for two time-offlight diffractometers designed for polycrystal analysis. HRFD is a highresolution Fourier diffractometer of the IBR-2 reactor; the pulse width  $\Delta t_0$ is determined by the rotational speed of the chopper and does not depend on the neutron wavelength. HRPD is the ISIS diffractometer;  $\Delta t_0$  depends on the neutron moderation and, in the first approximation, is proportional to the wavelength.

The expressions for the geometric terms in Eqns (20) and (21) are valid if the characteristic sizes of both the moderator and the detector are not large and their surfaces are perpendicular to the average paths in primary or scattered beams. Otherwise, terms containing  $\Delta L/L$  and changing  $\Delta t_0/t$  appear. As a result, the so-called time-focusing condition is possible to realise; that is, if the incidence angles of a moderator  $\alpha_1$  and a detector  $\alpha_1$  and the distances  $L_1$  from the moderator to the sample and  $L_2$  from the sample to the detector, respectively, satisfy equations

$$2\frac{L_1}{L}\tan\alpha_1\tan\theta_0 = 1, \qquad 2\frac{L_2}{L}\tan\alpha_2\tan\theta_0 = 1, \qquad (22)$$

then, in the first approximation, the geometric term is eliminated from Eqns (20) and (21). Conditions (22) conform to the fact that the overall time-of-flight of a neutron depends on the product  $L \sin \theta$  which can be made constant for neutrons of different wavelengths by the selection of angles  $\alpha_1$  and  $\alpha_2$ .

The time-focusing method for time-of-flight diffractometers had been independently and almost simultaneously proposed by J Carpenter [61] and A Holas [62] and was first realised at the IBR reactor in Dubna [63]. In polycrystal experiments, this method offers a substantial (approximately 5-fold) improvement in the luminosity of a diffractometer without an apparent impairment of its resolution; the method still remains to be widely used. In case of a large-area detector, the differential equation

$$\frac{\mathrm{d}L}{L} + \frac{\mathrm{d}\theta}{\tan\theta} = 0$$

is used to find the focusing surface, instead of the linear conditions (22).

Following the appearance of position-sensitive detectors providing high spatial resolution and multielement detector systems, 'electronic focusing' has come in use which consists in the independent recording of diffraction spectra by individual detector elements and the summation of readings with an appropriate shift along the time coordinate.

Time-focusing of neutrons after their diffraction at the crystal allows the contribution of the geometric term to the resolution function to be significantly reduced and the resolution of a time-of-flight diffractometer improved, but it does not affect  $R_t$ . There are two ways to diminish this part of the full resolution function which are self-evident from the expression for  $R_t$ :

$$R_t = \frac{\Delta t_0}{t} = \frac{\Delta t_0}{252,778L\lambda}, \qquad (23)$$

where  $\Delta t_0$  is the pulse width of a neutron source, as before (in µs), *L* is the flight path (in m),  $\lambda$  is the neutron wavelength (in A), the number 252.778 is the neutron mass to Planck constant ratio. It is possible to lessen  $R_t$  by decreasing  $\Delta t_0$  and increasing the flight distance. Both these factors were taken into account in the construction of a HRPD for the ISIS source in Great Britain, now one of the best time-of-flight diffractometers in the world [51]. By virtue of the small pulse width of fast neutrons from the source and a special design of the moderator, the width of the thermal neutron pulse is about 15 µs A<sup>-1</sup> which in turn allows to have  $R_t$  values of up to 0.0006, at  $L \sim 100$  m. Neutron diffractometer with so high resolution in terms of *d*-spacing is but slightly inferior to the best similar instruments on up-to-date synchrotron sources.

Unfortunately, the above method for improving the timeresolution of time-of-flight diffractometers leads to a significant loss of their luminosity. The index of this loss is a sum of incomplete neutron slowing down in a thin moderator, cutoff of a few source pulses to prevent neutron recycling on a large flight path, and losses in the solid angle; it amounts to 15-20.

This mode of achieving high resolution is altogether unacceptable for LPS. For example, the flight path must be in excess of 1 km if the resolution  $\Delta d/d = 0.001$  is to be reached for the IBR-2 reactor. In such cases, methods of correlation analysis proved to be very effective (first and foremost, neutron Fourier diffractometry).

### 4. Neutron Fourier diffractometry

Fourier diffractometry is a correlation method for the spectral analysis of neutrons scattered by the sample. Correlation methods do not imply time-of-flight measurements for each detected neutron; instead, they estimate the probability for the recorded neutrons to be distributed by times-of-flight. Both correlation methods currently in use (there is the pseudostatistical method besides the Fourier method) were introduced almost simultaneously and developed in parallel. The technical and conceptual problems inherent in their realisation have for a long time precluded as wide application of them as that of traditional methods even though several studies yielded interesting results in certain special cases, in the first place in the presence of a strong statistical background. The development of the reverse time-of-flight technique by Finnish scientists and investigations with the SFINKS diffractometer at Gatchina have demonstrated that only the Fourier method is compatible with the best existing diffractometers in terms of resolution and luminosity. It is a significantly higher luminosity of the Fourier method, as compared with that of the pseudostatistical method, that predetermined its successful development. Today, there are four working Fourier diffractometers and planning is going ahead for a few more devices. For this reason, the present review is concerned only with the Fourier method and does not touch upon the other correlation method used in time-of-flight neutron diffractometry.

### 4.1 Fourier chopper and the reverse time-of-flight technique

Fourier chopper of neutron beams consists of a rapidly rotating disk divided along the perimeter into sections alternately opaque or transparent to neutrons. Such a chopper generates a flux of neutrons in the form of periodic short (down to 7  $\mu$ s) pulses. Unlike other choppers, e.g. one-slit Fermi chopper, the Fourier chopper causes only moderate reduction of the flux but induces the recycling effect which accounts for the almost complete overlap of the recorded spectra. Discrimination between the overlapping spectra is accomplished by the substitution of the requirement to know the distribution of probabilities to detect neutrons for the requirement to know the exact time-of-flight of each recorded neutron. The former condition is far weaker than the latter and allows the problem to be solved if an additional degree of freedom is obtained.

Technically, the problem is reduced to determining the probability for a neutron to escape from the source some time ago, pass through the chopper, and reach the detector instead of recording the time of neutron entering the detector. This scheme was first proposed in 1972 [21] and is currently known as the reverse time-of-flight method. For illustration, let us consider a functional scheme of a Fourier time-of-flight diffractometer on a pulsed source (Fig. 5a). Its main units include a source of neutrons with moderator, Fourier chopper and data acquisition system in which correlation analysis of signals from the neutron source, chopper, and detector is performed. Figure 5 is a schematic representation of time-diagrams of neutron pulses from the source (Fig. 5b) and the triangular transmission function of the Fourier chopper (Fig. 5c) together with modulating binary signal sequences.

It turned out that by recording events when the speed of the chopper changes continually (in accordance with a certain law) and writing into the memory of the analyzer only those with a high probability of recording, one can obtain the distribution of elastically scattered neutrons by times-offlight from the chopper to the detector, that is the usual time-of-flight diffraction spectrum. The possibility of sorting out is ensured by the formation of pick-up signals coincident with the moments of the 'open' state of the reactor and the chopper and governing the work of the fast-shift register that serves to accumulate detector signals.

The differences of such working regime from that in the absence of a Fourier chopper are as follows:

(1) the recorded spectrum is 4 times less intensive (transmission of the chopper is about 0.25%);

Û

Pulsed

sourse

conv. units 0

1

0

Correlating electronics

Signal from

source

а

Sample

с

Detector

where D is the dispersion  $(D^{1/2} \approx 136 \text{ }\mu\text{s})$ . The statistical counting error in the time channel is totally determined by the quantity I(t) and equals  $I^{1/2}$ .

For a Fourier diffractometer on a source generating continuous fluxes, the relation for the intensity being measured looks like

$$I(t) \propto \int R_{\rm c}(t-\tau)\sigma(\tau)\,\mathrm{d}\tau + c \int \sigma(\tau)\,\mathrm{d}\tau + B(t)\,, \qquad (26)$$

where the shape of diffraction peaks is determined by the resolution function of the Fourier chopper  $R_c$  while the second integral is the so-called correlation background represented in this case by the sum of all detected neutrons. In the first approximation [64]

$$R_{\rm c}(t) \simeq \int_0^\Omega g(\omega) \cos \omega t \, \mathrm{d}\omega \,, \tag{27}$$

where  $g(\omega)$  is the distribution function of the chopper rotational speed and  $\Omega$  is the maximum frequency of neutron flux modulation by the Fourier chopper. Evidently, the width  $R_{\rm c}(t)$  is largely dependent on the  $\Omega$  value. For the Blackman frequency distribution,

$$g(u) = 1 + p\cos\pi u + q\cos 2\pi u \tag{28}$$

(where  $u = \omega/\omega_{\rm m}$ , p = 1.03, and q = 0.08) at  $\Omega = 150$  kHz,  $R_{\rm c} \sim 7 \ \mu {\rm s}$ , i.e. the diffraction peak width is about 46 times smaller than in the former case.

The situation for a Fourier diffractometer on a pulsed source is a combination of the two cases. For I(t), it is possible to write

$$I(t) \approx \pm \int R_{\rm s}(t-\tau)R_{\rm c}(t-\tau)\sigma(\tau)\,\mathrm{d}\tau + c\int R_{\rm s}(t-\tau)\sigma(\tau)\,\mathrm{d}\tau + B(t)\,,$$
(29)

where the first term defines the shape of narrow ( $W \approx 7 \,\mu s$ ) diffraction peaks while the second one is the correlation background in the form of broad maxima ( $W \approx 320 \,\mu s$ ).

The sign  $\pm$  in front of the first term arises due to the possibility to control the phase of a signal from the Fourier chopper. In case of parallel accumulation of functions  $I(t)_{\perp}$ and  $I(t)_{-}$ , their subtraction yields a high-resolution diffraction spectrum without broad maxima from the source (Fig. 6). The sum of  $I(t)_+$  and  $I(t)_-$  gives, with a high accuracy, dispersion of readings in the high-resolution spectrum.

An important feature distinguishing Fourier diffractometers on pulse and steady state neutron sources is the shape of correlation backgrounds represented by diffraction maxima with the width close to that of a neutron pulse from the source. In the case of a steady state neutron source, the correlation background of the Fourier diffractometer at each point of the spectrum equals the total number of neutrons counted during the period of recording, i.e. it shows no functional time-of-flight dependence. The following line of reasoning appears appropriate in comparing correlation



b

Signal from detector

Signal from

Fourier chopper

chopper

0.5

0

1

(2) the diffraction peak width is approximately equal to the inverse maximum modulation frequency of the beam;

(3) there is effect of correlation between the neighbouring points of the spectrum.

It should be emphasised that only the Fourier method provides such a substantial (ca. 40-fold) improvement of resolution without a significant loss of luminosity. Indeed, had the improvement been achieved due to a longer flight path between the source and the sample, the luminosity would have dropped by more than 100 times.

The mathematical substantiation of the method is given in Refs [64-66]. Here is only a brief summary of situations arising when a time-of-flight diffractometer and a Fourier diffractometer at steady state or pulsed neutron sources are used.

In the general case, time dependence of the intensity of neutrons elastically scattered at the sample (one-dimensional time-of-flight spectrum) may be written in the form of two items

$$I(t) \simeq \int R_{\rm s}(t-\tau)\sigma(\tau)\,\mathrm{d}\tau + B(t)\,, \tag{24}$$

where  $\sigma$  is the scattering cross-section (for a polycrystal, it is a sum of  $\delta$ -like distributions corresponding to Bragg diffraction peaks),  $R_s$  is the diffractometer resolution function, B is the background intensity. In all three cases to be examined,  $R_s(t)$ is a convolution of a certain set of distributions which take into account the broadening of the diffraction peak related to both time and geometric (angular) uncertainties of the scattering process. However, to make the comparison clear, let us tentatively assume that the geometric contribution is small and examine only the time portion of resolution functions.

For a time-of-flight diffractometer on a pulsed source,  $R_{\rm s}(t)$  is the convolution of the function describing a fast neutron pulse with the response function of the moderator and represents (e.g. for IBR-2) a slightly asymmetric distribution close to a Gaussian with the width of 320 µs at half maximum. For coherently scattering samples, the back-



**Figure 6.** A part of a neutronogram from  $La_2CuO_4$  in a time-of-flight interval corresponding to the interval *d* from 1.273 to 1.427 A with two adjoining peaks measured at a Fourier diffractometer. The figure shows spectra measured in parallel with two analyzers and consisting of a broad maximum and narrow ones (a). Summarised readings by the two analyzers give dispersion for the high-resolution spectrum formed when spectrum (2) is subtracted from spectrum (1). The peak width in the dispersion spectrum (b) roughly corresponds to the pulse width of the neutron source, and the high-resolution peak width (c) — to the resolution function of the diffractometer (0.00144 in the given case).

backgrounds for steady state and pulsed sources. If the spectrum of neutrons from a source is of Maxwell's shape, the correlation background in the absence of an additional filtration in a steady state reactor equals

$$B_{\rm sr} = \text{const} \sim S_{\rm tot} \sim \int_0^\infty \Phi(\lambda) \,\mathrm{d}\lambda$$
$$= \int_0^\infty 2\Phi_0 \frac{\lambda_0^4}{\lambda^5} \exp\left(-\frac{\lambda_0^2}{\lambda^2}\right) \,\mathrm{d}\lambda = \Phi_0 \,, \tag{30}$$

where  $\Phi_0$  is the full neutron flux and  $\lambda_0 = 1.8$  A is the characteristic wavelength. The correlation background for a pulse reactor may be written as

$$B_{\rm pr} = B(\lambda) \simeq \int_{\Delta\lambda} \Phi(\lambda) \, \mathrm{d}\lambda = 2\Phi_0 \frac{\lambda_0^5}{\lambda^5} \exp\left(-\frac{\lambda_0^2}{\lambda^2}\right) \frac{\Delta\lambda}{\lambda_0} \,, \ (31)$$

where the integration interval  $\Delta \lambda$  is determined by the width of the resolution function  $R_s(t)$  and approximately equals  $0.02\lambda_0$ . Other things being equal, the quantity

$$G \simeq \left(\frac{B_{\rm sr}}{B_{\rm pr}}\right)^{1/2} \simeq 5 \left(\frac{\lambda^5}{\lambda_0^5} \exp \frac{\lambda_0^2}{\lambda^2}\right)^{1/2} \tag{32}$$

defines a decrease in the statistical error due to the pulse nature of the neutron source. In other words, the effect (highresolution peak intensity) to background ratio is significantly higher for a Fourier diffractometer at a pulsed neutron source especially in low-intensity regions of the primary neutron spectrum (at wavelengths far from the maximum of primary neutron distribution by  $\lambda$  which is normally close to the Maxwellian distribution). For this reason, the use of Fourier diffractometry for precision measurements is more promising in combination with pulsed sources. On the other hand, a survey of 'moderate complexity' samples using Fourier diffractometry in conjunction with continuous flux sources offers additional opportunities as compared with other approaches due to the advantages of the time-of-flight method [67–69].

As far as pulsed neutron sources are concerned, Fourier diffractometry opens totally new prospects, viz. high-resolution high-flux diffractometry for LPS and moderation optimisation in terms of neutron beam intensity and a marked decrease in the flight path for SPS.

Good prospects for using Fourier diffractometry in combination with different neutron sources are illustrated by Table 3. Apart from crystallographic studies, the method appears promising for internal stress investigations in various materials. Its unique potentialities were demonstrated with a specialised Fourier diffractometer (Fourier Stress Spectrometer) designed for internal stress measurements [24, 70]. The first experiments to this effect were carried out using the highresolution Fourier diffractometer of the IBR-2 reactor [71, 72].

A study assessing the possibility to employ the Fourier method for neutron spectroscopy has recently been reported in Ref. [73]. This interesting line of research is worth special consideration.

 Table 3. Prospects of using Fourier diffractometry with different neutron sources\*

Source	Diffraction					
	Crystallography	Internal stress				
Steady state	Promising resolution ~ 0.003 moderately complicated structures	Very promising resolution 0.003-0.005				
LPS	Very promising resolution ≤ 0.001 medium and low-symmetry structures	Very promising resolution 0.003-0.005				
SPS	Selected studies	No prospects				
* LPS — Long Pulse Sources; SPS — Short Pulse Sources						

### 4.2 High-resolution Fourier neutron diffractometer

Let us consider the high-resolution Fourier diffractometer (HRFD) at the IBR-2 reactor to illustrate all the possibilities provided by the method. Moreover, this may give an idea of the construction of modern facilities used in neutron scattering studies.

HRFD is a product of concerted efforts of JINR, PIYaF, and VTT, Finland, which took into account the experience of working with the first Fourier diffractometer SFINKS at the steady state reactor at Gatchina [23]. The neutron beam was obtained early in 1992, and the first high-resolution measurements of diffraction spectra were made in June 1992 [25] (Fig. 7).



**Figure 7.** Comparison of neutron diffraction pattern from a  $YBa_2(Cu,-Fe)_3O_{6.3}$  (Y123) powder measured in the high-resolution regime on a HRFD (a) and with the resolution normal for a diffractometer at the IBR-2 reactor (b). Primes indicate estimated positions of the diffraction peaks.

The HRFD (Fig. 8) is mounted on the beam tube No. 5 of the IBR-2 reactor equipped with a water comb-like moderator. Just behind the biological shielding, there is a mechanical filtering chopper which suppresses the fast neutron and  $\gamma$ -ray background between power pulses of the reactor; also, there is an auxiliary metallic neutron-guide and a segment of the straight neutron-guide tube with a window  $30 \times 200 \text{ mm}^2$  in cross-section.

The Fourier chopper is placed behind the second shielding. It consists of a rotating disk 540 mm in diameter on the engine shaft and a plate of the stator on a stationary platform. The disk and the plate are of a Ti–Zr alloy with the zero coherent scattering length. The disk has 1024 radial slits cut along the periphery and filled with  $Gd_2O_3$ , each one being 60 mm in length and 0.7 mm in mid-width. The stator plate contains similar slits. The chopper is run by a two-pole asynchronous motor with an axially fixed incremental optical coding sensor to measure the speed and acceleration of the disk and to form pick-up signals to be received by the timeanalyzer. The motor is fed through a controlling drive having an in-built microcomputer. The computer processes information about the speed and acceleration of the disk.

A neutron beam on a sample is shaped by a curved neutron-guide tube of 30 mm thick <sup>58</sup>Ni-coated high-quality glass. The 19 m neutron-guide tends to be conical in both horizontal and vertical planes and has the input and output windows of  $30 \times 200$  and  $10 \times 100$  mm<sup>2</sup> respectively. The flight path between the disk and the sample is 20000 mm.

The HRFD detecting system consists of a high-resolution scintillation <sup>6</sup>Li-detector placed at a mean scattering angle 152° and connected with correlation electronics and two <sup>3</sup>Hedetectors. The main detector ensures time-focusing during diffraction. It has six detector elements, each containing a prism (lightguide) and a photomultiplier behind it. Each prism has 4 or 6 faces with 1 mm wide NE-912 <sup>6</sup>Li-glasses stuck to them. The glass length varies from 100 to 150 mm. The full solid angle of the detector is 0.08 sr. The contribution of the detector to the geometric term of the resolution function does not exceed 0.0003 if the adjustment is correct (see Ref. [74]). The additional He-detectors ensure ordinary resolution. One of them is a linear position-sensitive detector with a high-resistance anode wire. It is mounted on a rotating platform and may be used in the scattering angle range from  $0^{\circ}$  to  $45^{\circ}$  to record diffraction maxima with large  $d_{hkl}$ (> 10 A).



Figure 8. The scheme of a HRFD at the IBR-2 reactor. Distances are in mm.

The storage electronics for high-resolution spectra includes three analyzers with specially designed polar correlators. One of them with 1024 channels is intended to record the autocorrelation function while two others (each having 8196 channels) — to record diffraction spectra with positive and negative phases of pick-up signals from the Fourier chopper (see Ref. [75] for more details). The analyzers are connected with PC/AT-386 via an in-line BITBUS interface. The storage electronic equipment for diffraction spectra from the <sup>3</sup>He-detectors and the systems controlling temperature, step engines, and other units of HRFD are CAMAC modules.

One of the most difficult task encountered in working with a HRFD is the description of the shape of diffraction peaks. Their shape depends on the frequency distribution  $g(\omega)$ , the phase adjustment of the pick-up signal from the Fourier chopper (to ensure the coincidence of the signal front with the time when slits on the rotor pass across those on the stator), and correlation phenomena related to the registration of information [76]. One of these phenomena arising from the correlation of readings in adjoining channels of the analyzer is the appearance of small negative gaps in the high-resolution spectrum. A two-sign peak shape model is employed to take them into consideration in spectra processing by the Rietveld method (see Section 6.1). As a rule, such a model is an isolated diffraction peak measured with good statistics from the spectrum of the sample being examined or the standard polycrystal spectrum.

The first term  $R_t = \Delta t_0 / t$  in the expression for the HRFD resolution function (21) is determined by the effective width of a pulse from the Fourier chopper and the flight path between the chopper and the detector. It can be written as  $R_t = 6/(Vd)$ , where V is the rotational speed of the Fourier chopper (in rpm) and d is the interplanar distance (A). In the standard working regime and at d = 1 A, V = (4000 - 1)6000) rpm and  $R_t = 0.0010 - 0.0015$  respectively. The geometric component  $R_{\theta} = \Delta \theta / \tan \theta$  of the resolution function is determined by the primary beam divergence, sample size, and detector focusing conditions; it is 0.0010 when there is no collimator in front of a cylindrical sample 6 mm in diameter and 60 mm in height. The contribution to the resolution function related to the disk thickness of the Fourier chopper, the effective sample thickness, and the thickness of thee detecting elements does not exceed 0.0003. The full HRFD resolution function was measured using diffraction on highquality standard powders (Ge, Si, Al<sub>2</sub>O<sub>3</sub>) and single crystals. Its dependence on the interplanar distance is in good agreement with the calculated curve.

Diffraction spectra from HRFD are recorded at a constant time-analyzer channel width which is normally 4 µs. The 8196 channels of the analyzer correspond to the interval  $\Delta d_{hkl} = 3.16$  A which allows the diffraction spectrum to be concurrently recorded in the  $d_{hkl}$  range from 0.58 to 3.74 A at a 6000 µs delay following the pulse escape from the reactor.

The calibration of HRFD was carried out using standard samples. Specifically, the quantity  $L \sin \theta_0$  defining absolute values of elementary cell parameters of the crystals being examined was accomplished using the SRM-676 aluminium oxide powder (National Institute of Standards and Technology, USA) with the following parameters:  $a = (4.75919 \pm 0.00044)$  A,  $c = (12.99183 \pm 0.000174)$  A. The structural characteristics thus obtained z(Al) = 0.35224(6), x(O) = 0.30621(9),  $B_T(Al) = 0.24(1)$  A<sup>2</sup>,  $B_T(O) = 0.28(1)$  A<sup>2</sup>,

 $\chi^2 = 1.75$ ,  $R(F^2) = 0.054$  are in good agreement with those reported in the literature [77, 78].

When comparing the luminosity of Fourier diffractometers and conventional time-of-flight diffractometers, it is necessary to take into account effects of the correlation background. Let us introduce an additional factor  $k_{\rm f}$  into the expression for the luminosity J used to be written as the product of the full neutron flux on a sample in the working wavelength interval  $\Phi_0$ , the feasible 'effective' area of the flux cross-section S, and the solid angle of the detecting system  $\Omega_{\rm d}$ :  $J = \Phi_0 S \Omega_{\rm d}$ . The correlation factor depends on the relationship between the pulse width and diffractometer resolution, individual sample features, and certain experimental parameters. It follows from the experience of operating the available Fourier diffractometers that  $k_{\rm f} \approx 0.01-0.1$  and  $k_{\rm f} \approx 0.1-1$  for steady state reactors and IBR-2 respectively.

The principal characteristics of HRFD and diffractometers of the same class at other neutron sources are compared in Table 4.

 Table 4. Characteristics of high-resolution power diffractometry with different types of neutron sources

Parame- ters *	D2B ILL France	HRPD RAL UK	SFINKS PINF RAS Russia	FSS GKSS Germany	HRFD JINR Russia
$\lambda \\ \Phi \\ S \\ \Omega \\ R  imes 10^4$	1.4-5.7	0.8-4	0.9-4	0.9-4	0.9-12
	$10^{7}$	2 × 10 <sup>6</sup>	1 × 10 <sup>7</sup>	1 × 10 <sup>6</sup>	$1 \times 10^{7}$
	5	2	5	5	2
	0.008	0.1	0.1	0.11	0.08
	5	5	20	20	5

\*  $\lambda$ , A — the working wavelength range;  $\Phi$ , n cm<sup>-2</sup> s<sup>-1</sup> — the neutron flux at the sample site; S, cm<sup>2</sup> — the maximum 'effective' sample cross-section;  $\Omega$ , sr — the solid angle of the detector assembly;  $R = \Delta d/d$  — the maximal resolution of the diffractometer

# 5. Single crystal studies using time-of-flight diffractometers

Problems to be solved with the help of single crystal time-offlight diffractometers may arbitrarily be divided into two categories: the classical analysis of atomic and magnetic crystal structures and experimental analysis of the reciprocal lattices point shape and the intensity distributed over intersite space. In the former case integrated intensities of a large number of diffraction peaks are measured and further analysis is carried out at the level of  $I_{int}$  defined by Eqn (9). In the latter case, continuous reciprocal space scanning is needed for which purpose the use of a time-of-flight diffractometer appears to provide an especially effective means.

**5.1 Structural analysis with a time-of-flight diffractometer** Monocrystal structural studies using time-of-flight diffractometers developed slower than investigations along other lines although the first attempts date to the late Sixties. Early experiments largely tested procedures for measuring  $I_{int}$  and introducing necessary corrections for the transition to structure factor moduli.

Reference [79] reports a  $Mn_5Ge_3$  structural study conducted on the Harwell pulsed source with the mean power of 1 kW. Because of the low neutron flux, a relatively large single crystal had to be used ( $8.3 \times 3.8 \times 2.7 \text{ mm}^3$ ) which resulted in high extinction. The authors failed to find a proper way to take it into account and chose to measure the same structure factors at several scattering angles (hence, at different wavelengths). Having introduced corrections for the effective neutron spectrum and absorption, they performed linear extrapolation of the experimentally found values of structure factors  $F_{exp}$  to the zero wavelength. The quantities thus obtained turned out to be in good agreement with the calculated ones. A similar but more detailed study was carried out on the IBR pulse reactor using deuteronaphthalene  $C_{10}D_8$ crystals [80]. The authors suggested and realised a special procedure for taking into consideration the effective neutron spectrum and used the Zachariasen approximation to take into account the extinction. Experimentally found structure factors of  $C_{10}D_8$  were compared with  $F_{cal}$  inferred from the data published in Ref. [81]. The agreement between them was evaluated using the conventional *R*-factor

$$R_F = \frac{\sum |F_{\exp} - F_{cal}|}{\sum |F_{\exp}|}, \qquad (33)$$

where the summation is over all measured sets of Miller indices. The total of about 100 reflections were measured in Ref. [80], and the acceptable value of 5.2% was obtained for  $R_F$ . The authors concluded that their method provided  $F_{exp}$  values sufficiently accurate to solve a wide range of problems pertaining to the crystal structure analysis.

The first single crystal study using a time-of-flight diffractometer that yielded new structural information appears to have been conducted at Dubna [82]. This study analysed the structure of deuterated lanthanum-magnesium nitrate  $La_2Mg_3(NO_3)_{12} \cdot 24D_2O$  (LMN) and specified coordinates and isotropic thermal factors of deuterium atoms. Comparison of these findings with previously obtained results of X-ray crystal analysis revealed regular changes of all hydrogen bonds associated with a mean 0.2 A shift of the centre of gravity in a hydrogen (deuterium) electron cloud towards the atom to which it is bound. Figure 9 gives an idea of the value of these data in terms of precision showing a forked hydrogen bond in the LMN structure.



**Figure 9.** The environment of one of the hydrogen atoms in the LMN structure. Position P corresponds to its X-ray coordinates and position P' — to neutron coordinates. O — positions of the nearest oxygen atoms. Distances are given in A.

Since then, there has been great progress in single crystal structural studies using time-of-flight diffractometers in terms of both the luminosity and the precision of experimental data. For example, a study of a Bi<sub>2</sub>(Sr,Ca)<sub>3</sub>Cu<sub>2</sub>O<sub>8+ $\gamma$ </sub> single crystal having dimensions  $1.5 \times 1.0 \times 0.03$  mm<sup>3</sup> with a DN-2 diffractometer at the IBR-2 reactor yielded a desired collection of data and provided for better understanding of the cause underlying modulation of the structure by the insertion of an additional oxygen atom into the BiO layer [83].

It has been shown above that the efficiency of measuring reflections from a single crystal with a time-of-flight diffractometer grows in proportion to the elementary crystal cell volume. It can therefore be expected that the analysis of organic and biological crystals with large  $V_{\rm c}$  will probably make the main structural problem to be solved with the help of single crystal diffractometers. Diffractometers with a monochromatic beam are used to study macromolecular crystals, e.g. protein crystals of myoglobin [84], trypsin [85], etc. However, the time needed for data collection (about 10<sup>3</sup> hours to record 10<sup>4</sup> reflections necessary to ensure spatial resolution of around 2 A) is close to the reasonable duration of a single experiment. According to simple estimates, this time may be reduced at least ten-fold using modern time-offlight diffractometers. There are already reports of measuring a few thousands of diffraction peaks within a reasonable timespan [86].

### 5.2 Continuous scanning of reciprocal space

Many single crystal diffraction studies have to analyse the site shape in a crystal reciprocal lattice and the intensity distributed over intersite space. The necessity of the analysis arises from such phenomena as transformational twinning of the crystal, formation of incommensurate modulated or helical magnetic structures, diffuse scattering caused by structural defects or correlated thermal atomic motion. Let us consider at greater length an experiment on a ferroelastic crystal which illustrates specific features of the problems in question and the potential of time-of-flight diffractometers.

Transformational twinning of ferroelectric and ferroelastic crystals on their transition to the low-symmetry phase may be described in general terms as the formation of the composite reciprocal lattice of a crystal [87] which is apparent in a diffraction experiment as peak splitting into constituent components. Determining characteristics of the components yields quantitative information about geometric parameters of the twins (domains) and changes of the domain structure under the influence of external fields. If peak splitting occurs in a certain plane of a reciprocal space, the integrated intensity distribution near the initial site of a reciprocal lattice may be represented as a sum of several (8)-like functions shifted along axes  $\xi$  and  $\gamma$ :

$$I_{\rm s}(\xi,\gamma) = \sum_{i} r_i I(\xi - \xi_i, \gamma - \gamma_i) , \qquad (34)$$

where  $I_s$  is the intensity being measured,  $r_i$  stands for weight factors related to a fraction of the *i*-th domain type in the sample, and  $(\xi_i, \gamma_i)$  is the position of the *i*-th component. The experimentally found positions of the components can be associated with coordinate points in reciprocal space, i.e. there is the possibility to determine the spontaneous shift angle, the linear deformation of the lattice, etc.

Specifically, this method was used in Ref. [88] to study characteristics of the domain structure in KD<sub>2</sub>PO<sub>4</sub> (DKDP) crystals undergoing phase transition from tetragonal to orthorhombic phase at 214 K, with  $\Delta a = -\Delta b \approx 0.055$  A. Also, this transition may be described as the emergence of a monoclinic cell due to displacements in coordinate directions. In this case, the transition parameter is the spontaneous shift angle  $u_{xy}$ . In accordance with the scheme of formation of a composite reciprocal lattice, reflections of the [h00]-type split into three and all other reflections into four components. This inference is supported by the measured intensity distribution around the (220) lattice point shown in Fig. 10. It is easy to calculate from the magnitude of splitting the transitioninduced changes in cell parameters and the spontaneous shift angle which proved to be 31.3 angular minutes for DKDP. The intensity of individual site components characterises the relative number of domains of different orientation.



**Figure 10.** Experimental intensity distribution at site (220) of a KD<sub>2</sub>PO<sub>4</sub> crystal at T = 80 K. At this temperature, the crystal is in the low-symmetry phase; transition to this phase was associated with the breakup of the reciprocal lattice sites into constituent components due to crystal twinning. *x* axis labels the neutrons' time-of-flight (time-analyzer channels), *y* axis corresponds to the scattering angle (position groups of the one-dimensional PSD). The whole intensity distribution has been obtained by the parallel recording technique.

The reciprocal space volume in which  $I_s$  is distributed, i.e. the one to be analysed, is normally easy to observe with a time-of-flight diffractometer equipped with a detector the linear dimension of which exceeds 50 cm. The overall distribution being measured by the parallel recording technique, its conspicuous advantage over point-scanning in terms of time consumption is easy to perceive bearing in mind that the number of points to be scanned amounts to several thousands. Moreover, constant orientation of the crystal throughout the measuring procedure is an important factor facilitating data processing.

An example of using a time-of-flight diffractometer in diffuse scattering experiments is provided in Ref. [89] which reports data on thermal scattering distributed near reciprocal lattice sites in crystals of  $Sr_xBa_{1-x}Nb_2O_6$  (SBN-x) and (CH<sub>3</sub>NHCH<sub>2</sub>COOH)<sub>3</sub> · CaCl<sub>2</sub>. Moreover, SBN-x crystals were examined in terms of their disproportional structural modulation in course of transition ( $T_c \approx 350$  at x = 0.7) to the ferroelectric phase [90]. In both cases, parallel detecting of scattered neutrons greatly promoted the solution of the problems of interest.

## 6. Structural studies of polycrystalline substances using time-of-flight diffractometers

The difficulties offered by the solution of structural problems and the precision of data obtained with a diffractometer for polycrystals are first and foremost dependent on the resolution in terms of interplanar distance. If  $R(d) \approx 0.01$ , only atomic coordinates of rather simple structures can be specified. Also, it is sometimes possible to identify occupation factors and isotropic thermal parameters for individual atoms. Independent specification of atomic coordinates, occupation factors, and isotropic thermal parameters is feasible at the level of  $R(d) \approx 0.003$ . Finally, at  $R(d) \leq 0.001$ in a single crystal experiment, the accuracy of the result matches the structure complexity, both being almost invariably higher than those obtained in polycrystal studies using X-ray diffraction.

Today, the Rietveld method developed in late Sixties [91] is most extensively used to analyse polycrystal diffraction data.

### 6.1 The Rietveld method

The Rietveld method [92] introduces the parametric description of the intensity of the measured diffraction spectrum which allows the least square method and any other technique for functional minimisation to be employed to determine crystal characteristics of interest. The functional of parameters is normally written as

$$\chi^2 = \sum_{i} \omega_i (I_{\exp,i} - I_{\operatorname{cal},i})^2 , \qquad (35)$$

where  $\omega_i$  is the weight of the *i*-th point and  $I_{exp}$  is the intensity measured in the sample and corrected for the effective spectrum and absorption,  $I_{cal}$  is calculated value of intensity; the sum is taken over points of the measured spectrum in an interplanar distance interval  $d_i$ .  $I_{cal}$  is calculated using a (10)-like formula

$$I_{\text{cal}}(d_i) = C \sum_{hkl} j_{hkl} |F_{hkl}|^2 d_{hkl}^4 \, \varphi(d_{hkl} - d_i) + I_{\text{b}}(d_i) \,, \quad (36)$$

where *C* is normalisation constant,  $d_{hkl}^4$  is the quantity proportional to the Lorentz factor,  $\varphi$  is the function describing the diffraction peak shape, and  $I_b$  is the background intensity. All characteristics of crystal atoms are incorporated in structure factors  $F_{hkl}$  which are calculated in the approximation isotropic in thermal vibrations according to Eqn (4):

$$F_{hkl} = \sum_{j}^{N} b_j r_j \exp\left[2\pi i(hx_j + ky_j + lz_j)\right] \exp\left(-\frac{B_j}{8d_{hkl}^2}\right), \quad (37)$$

where  $b_j$  stands for coherent scattering lengths,  $r_j$  is the factor determining the number of *j*-type atoms in a cell (it can also serve as a parameter taking into account position occupation, if necessary),  $(x, y, z, B)_j$  are the relative coordinates and thermal parameter of the *j*-th atom. Parameters being specified when the functional (35) undergoes minimisation include sets  $(r_j, x_j, y_j, z_j, B_j)$ , the background intensity (normally described by a polynomial of a degree not higher than fourth), and elementary crystal cell parameters included in the expression for  $d_{hkl} = 1/H_{hkl}$ .

The experience in structural analysis of polycrystal diffraction data by the Rietveld method indicates that, if *R* shows weak dependence on  $d_{hkl}$ , the number of peaks to be reasonably considered is approximately  $(3R)^{-1}$  for structures with the medium symmetry level. Assuming that the number of peaks must be 5 times that of the parameters being specified, it appears that up to 70 structural parameters (i.e. atomic coordinates, occupation factors, and thermal parameters) can be simultaneously specified if R = 0.001.

#### 6.2 Examples of structural studies

The structural data quality resulting from high-resolution time-of-flight diffractometer studies may be evaluated from the following example [93]. The structure of deuterated benzene C<sub>6</sub>D<sub>6</sub> [the space group Pbca, a = 7.3551(3) A; b = 9.3712(4) A; c = 6.6694(3) A; V = 461.75 A<sup>3</sup> was inferred from a neutron diffraction pattern obtained on HRPD (ISIS). The measurements were made at T = 4.2 K using a sample 5 cm<sup>3</sup> in volume for 9 hours. The authors were interested in a part of the spectrum in the  $d_{hkl}$  range from 0.606 to 1.778 A consisting of 5382 points and containing 1040 diffraction peaks. Eighteen position and 36 anisotropic thermal atomic parameters were considered. Mean square deviations of coordinates were  $(1-2) \times 10^{-4}$ , corresponding to absolute errors in C-C and C-D bond lengths from 0.002 to 0.003 A. Both position and thermal parameters turned out to be in good agreement with the data obtained in a single crystal study of the same substance. It should be borne in mind that labour consumption in the polycrystal experiment was at least an order of magnitude lower than in the single crystal one.

References [67, 69, 94] offer examples of structural studies performed with the use of Fourier diffractometers. Reference [94] reports the HRFD structural analysis of a high-temperature superconductor Y123 with 10% of Cu atoms substituted by Zn atoms. The experiment was carried out on two identical samples one of which was enriched in <sup>65</sup>Cu (99%). The precision of the structural information thus obtained and simultaneous processing of the data on the two samples ensured highly accurate characterisation of Cu site occupation by Zn atoms in Cu–O chains and CuO<sub>2</sub> planes of the Y123 structure; also, there was evidence of the transition of a small positive charge from the chains to the planes following Zn substitution for Cu.

An important outcome of the high resolution of modern time-of-flight diffractometers for polycrystals is the possibility to obtain realistic experimental values for a large number of structure factors which in turn provides an opportunity to construct cross-sections for scattering density syntheses in accordance with Eqn (5). This is of special value for the identification of poorly occupied sites, i.e. when the Rietveld method is likely to yield misleading information due to the inevitable presence of systematic errors.

For example, specification of the HgBa<sub>2</sub>CuO<sub>4+ $\delta$ </sub> (Hg-1201) structure by the standard Rietveld method gave evidence of the presence of an additional superstoichiometric oxygen atom localised by the middle of the Hg plane edge. A HRFD experiment conducted at Dubna revealed rather a large number of experimental structure factors and allowed to construct scattering density maps for Hg-1201 [95]. Figure 11 shows a scattering density map for one of the cross-sections of an elementary cell of the compound. The peak amplitude corresponding to the O3 oxygen atom at a concentration of  $\delta = 0.12$  is 5 times the background peak amplitude. This means that atoms with the coherent scattering length close to that of oxygen (e.g. carbon) would be identified at a concentration of about 3%.

#### 6.3 High pressure experiments with microsamples

The sphere of application of neutron methods to studies on substance behaviour under high pressure has until recently been limited to a range of several GPa because rather large sample volumes ( $\sim 1 \text{ cm}^3$ ) were used in pressure cells of the piston-cylinder type. Diamond and sapphire anvils widely



**Figure 11.** Scattering density synthesis in the cross-section (x = 0.5,  $0 \le y \le 1$ ,  $0 \le z \le 0.5$ ) of an elementary cell of HgBa<sub>2</sub>CuO<sub>4+ $\delta$ </sub> with  $\delta \approx 0.12$  using experimentally obtained  $F_{hkl}$ . Peak O3 corresponds to the oxygen position in the centre of the structure's basic density occupied with the 12% probability. Amplitudes of the background peaks are approximately 5 times smaller than the amplitude of peak O3.

used with X-ray and synchrotron radiation sources were believed to be utterly impracticable because of small  $(1-10^{-2} \text{ mm}^3)$  sample volumes and relatively weak fluxes from neutron sources. However, a new method for high pressure neutron studies has been developed during the last decade based on the combination of the anvil technique and high-transmission low-background neutron diffractometry which allows the pressure range in these experiments to be extended to several tens of GPa [96]. The experience gained in the Kurchatov Institute was extrapolated to IBR-2 studies; in 1964, first experiments were carried out with the DN-12 diffractometer. Thorough handling of the neutron beam and an original design of the detecting system allowed for the use of the smallest sample and the highest pressure so far reported in the literature [97]. Figure 12 shows one of the measured diffraction spectra from a sample having as small a volume as 0.027 mm<sup>3</sup>. A series of interesting experiments were performed on the DN-12 diffractometer including a study with a superconductor HgBa<sub>2</sub>CaCu<sub>2</sub>O<sub>6+ $\delta$ </sub> [98], a NH<sub>4</sub>Cl molecular crystal [99], etc.

Another approach was realised by a French-English group using the ISIS and LANSCE sources [100] where the desired pressure was produced by a small-size 250 ton press with a tungsten carbide toroid cell. The group managed to raise pressure to 12 GPa using a 100 mm<sup>3</sup> sample and even to 26 GPa when the sample volume was reduced to 35 mm<sup>3</sup> and a cell of cemented diamond was used. At present, a similar chamber suggested in Ref. [101] is being prepared for IBR-2 diffraction experiments.

Bearing in mind that such pressures are possible to produce in a broad temperature range and there is every opportunity to further improve the available facilities, it is



**Figure 12.** The diffraction spectrum of a  ${}^{164}\text{DyD}_3$  powder in diamond anvils measured during 24 hours. The sample volume is 0.027 mm<sup>3</sup>, the pressure is 9.5 GPa. The figure shows Miller indices of the diffraction peaks from DyD<sub>3</sub> and the background peaks from the high-pressure cell (b).

safe to conclude that high pressure diffraction studies with pulsed neutron sources are much more promising than similar investigations on steady state reactors.

# 7. Investigations of irreversible transient processes in crystals

Specific features of neutron diffraction make it a valuable tool for gaining deeper insight into transient processes in condensed media. This issue has only recently become a matter of special interest, but the so-called RT (real time) experiments reported in the literature till now appear to give rise to a new branch of neutron diffraction, RT diffractometry, that is the use of neutron scattering to observe structural transformations at the atomic level straight in the course of their measurement. This approach implies recording both neutron diffraction and small-angle (diffuse) scattering although the majority of experiments examine only diffraction spectra as the most intensive component of scattering. Compared with diffraction of X-ray and synchrotron radiation which is equally often employed to survey transient processes, the RT neutron diffraction has all the advantages of using neutrons including the most valuable of them, i.e. the possibility to 'see' light atoms in the vicinity of heavy ones and distinguish between isotopes. Another important advantage extensively used in RT experiments is high penetrating ability of neutrons.

The scale of characteristic times which are possible to examine depends on whether the process can be reproduced or not. In the case of an irreversible process, e.g. a chemical reaction, the possibility to observe it is determined by the condition  $t_s \ll \tau$ , where  $\tau$  is the characteristic time and  $t_s$  is the time of measuring a single spectrum with the level of statistics sufficient for the purpose of the experiment. Naturally, RT diffractometry may be regarded as a self-contained technique only if  $\tau$  is not too large.  $t_s$  depends on the neutron flux in a primary beam, the surface area and scattering capability of the sample; it is 5-15 min for the most effective high-transmission neutron diffractometers coupled to steady state reactors. Similar  $t_s$  values have been obtained with certain pulsed neutron sources (ISIS, LANSCE). The IBR-2 reactor

producing the most intensive pulse flux offers the possibility to analyse irreversible processes in crystals with as high timeresolution as 1 min or better. For instance, one of the first experiments on Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> (a cement component) hydration [102] at  $t_s = 10-40$  s yielded important new information about the initial stage of the reaction whereas in earlier experiments conducted in ILL,  $t_s$  was 6-12 min.

Now, let us consider the experimental procedure and examples of irreversible processes investigated with IBR-2.

### 7.1 Time-of-flight diffractometer

### for transient process studies

The number of neutrons recorded by a detector for unit time in a scattering experiment may be roughly presented as

$$I = \Phi_{\rm o} S \, \frac{\Omega_{\rm d}}{4\pi} \, \delta \,, \tag{38}$$

where  $\Phi_0$  is the full neutron flux on the sample in the working range, *S* is the sample's surface area, and  $\delta$  is its scattering capability. The neutron flux in the IBR-2 diffractometers is  $10^7 \text{ n cm}^{-2} \text{ s}^{-1}$ , and the solid angle of the detecting system is easy to make 0.1 sr. The surface area and scattering capability being 5 cm<sup>2</sup> and  $\delta \approx 0.1$  respectively, the overall count rate is likely to be as high as  $5 \times 10^5 \text{ n s}^{-1}$ . This is a very high value which allows measurements to be made with the timeresolution  $t_s$  of around one minute and even seconds. The question is how 'useful' the detected neutrons are, i.e. what is the informative value of measured neutron spectra. 'The usefulness' is first and foremost determined by the breadth (or sufficiency) of the range of simultaneously recorded  $d_{hkl}$ and the resolution of the diffractometer.

For a large class of transient processes lending themselves to investigation with the help of neutron diffraction, e.g. chemical reactions in the solid phase, hydration and dehydration of biomolecules, isotope exchange, etc., a moderate resolution of the diffractometer is acceptable (of the order of  $\Delta d/d \approx 0.005 - 0.01$ ). On the contrary, a broad  $d_{hkl}$  range becomes of greater importance. It has been shown in Refs [103, 104] that time-of-flight diffractometers optimally meet these requirements for it makes moderate resolution feasible at relatively short flight paths (10-20 m) thus allowing for a higher neutron flux on the sample whereas the necessary  $d_{hkl}$ range is easy to obtain with several detectors placed at different scattering angles. Moreover, the installation of additional detectors at small angles ( $\sim 1^{\circ} - 3^{\circ}$ ) facilitates simultaneous recording diffraction and small-angle neutron scattering spectra, the latter yielding information about evolution of large-scale inhomogeneities in the scattering capability of the object being examined.

RT experiments are usually undertaken to study changes of an external parameter, e.g. temperature. In such cases, the time and temperature axes coincide, and continuous diffraction monitoring of temperature fluctuations of the structure is possible. If temperature changes are recorded much faster than diffraction spectra are measured, the time-resolution of monitoring structural changes is totally determined by the time required to achieve the necessary level of statistics ( $t_s$ ). This regimen is convenient to observe phase transformations in a system resulting from structural phase transitions or chemical reactions. Kinetic studies and the determination of characteristic constants (relaxation time, activation energy, etc.) are carried out using jump-like variation of external conditions.

### 7.2 Examples of studies

7.2.1 A chemical reaction in the solid phase. Given a simple reaction with a small number of intermediate phases, it is enough to follow the evolution of a few diffraction peaks measured at a fixed scattering angle. An RT experiment on  $YBa_2Cu_3O_x$  synthesis in the air with  $Y_2O_3$ ,  $BaCO_3$ , and CuO as the initial products required a much more sophisticated analysis [105]. The sample was placed in a large-volume muffle furnace with the wide input and output windows covered by neutron-transparent shields. The window size was sufficient to install several detectors at large and small scattering angles to record diffraction spectra in the interplanar distance range from 1 to 30 A. The sample was a mixture of the initial components stoichiometric for Y123 placed in a container of platinum foil. The initial sample weight was 10 g. The results reported in Ref. [105] have been obtained under conditions of a smooth temperature rise till it reached the maximum value of 940 °C. The temperature was maintained at this level for 6 hours and then gradually decreased to 160 °C (during ca. 3 hours). The resulting neutron diffraction patterns were consecutively analysed for the identification of the diffraction peaks, tracing their evolution, and structural analysis by the Rietveld method. It turned out that Y123 synthesis involved three stages: decomposition of the initial components, formation of intermediate phases, and synthesis of the final product. Kinetic analysis during the progress of the reaction demonstrated that it was well described by the equation for a reaction at twodimensional interphases.

7.2.2 Isotope exchange in a lipid membrane. The dependence of scattering probability on the isotope composition of a medium is one of the most important characteristics of interactions between neutrons and matter. A most demonstrative example is the interaction of hydrogen and deuterium having the coherent scattering lengths  $b_{\rm H} = -0.374$  and  $b_{\rm D} = 0.665$  (in  $10^{-12}$  cm units). A kinetic experiment based on a marked difference between  $b_{\rm H}$  and  $b_{\rm D}$  may be illustrated by the observation of the reversible substitution of H<sub>2</sub>O by  $D_2O$  in multilamellar lipid structures [106]. This study has shown that the substitution with a concurrent change of humidity is a complicated process involving many stages with different time-constants. In early experiments, the initial (fastest) stage proved impossible to observe, and its time constant was estimated to be about 1 min. Two further stages had characteristic times 3-4 and 10-30 min respectively. Their exact values depended on the initial and final humidity levels.

Reference [103] reports the observation of the initial stage. The glass sample  $(24 \times 24 \text{ mm}^2)$  was coated with oriented layers of a phosphatidyl choline and phosphatidyl glycerol mixture (1:1) and placed in a sealed chamber with windows of aluminium foil. Humidity was maintained by placing a cuvette with a cloth soaked with heavy or light water inside the chamber. One cuvette was replaced by another within approximately 1 s without the loss of sealing. It may be assumed that the D<sub>2</sub>O content in the sample during the H<sub>2</sub>O  $\rightarrow$  D<sub>2</sub>O substitution (or the H<sub>2</sub>O content in case of the backward substitution) obeys the exponential law, that is

$$m(t) = M\left[1 - \exp\left(-\frac{t}{\tau}\right)\right],\tag{39}$$

where t is the time elapsed since the initiation of the process, M corresponds to soaking water mass, and  $\tau$  is the character-

istic time of the process. Since the full structure factor of a lipid bilayer can be represented as a sum  $F_{\rm T} = F_{\rm L} + F_{\rm W}$ , where  $F_{\rm L}$  and  $F_{\rm W}$  are structure factors of aqueous and lipid entities respectively and  $F_{\rm W} \propto m(t)$ , the time-dependence of  $F_{\rm T}$  must also be exponential

$$F_{\rm T}(t) = F_{\infty} + F_1 \exp\left(-\frac{t}{\tau}\right),\tag{40}$$

where  $F_{\infty}$  and  $F_1$  are certain constants. In the absence of extinction effects,  $F_T \propto I^{1/2}$ , where *I* is the diffraction peak intensity, i.e. the dependence  $y(t) = \ln |F(t) - F_{\infty}|$  must be linear in time.

The experiment revealed time-dependence of the firstorder intensity of the reflection from the lipid multilayer  $(d \approx 40 \text{ A})$  with  $t_s = 2 \text{ s}$  within the first 250 s of the process. Figure 13 shows dependences m(t) for both processes which allow quantities  $\tau(\text{H}_2\text{O} \rightarrow \text{D}_2\text{O})$  and  $\tau(\text{D}_2\text{O} \rightarrow \text{H}_2\text{O})$  to be found as equalling 92 and 71 s respectively.



**Figure 13.** Time-dependences I(t) for the direct and backward  $H_2O \leftrightarrow D_2O$  substitution. Arrows indicate the beginning of the processes. Both processes are in good agreement with the exponential dependences with time constants 92 and 71 s.

7.2.3 Phase transition in heavy ice. When ice VIII was heated from the high-pressure annealed phase, it first transformed to the low-density amorphous phase lda, then to cubic ice Ic, and eventually (on further heating) to ordinary hexagonal ice Ih [107]. It was suggested that the low-density phase arose from the high-density one hda although the authors failed to observe this process.

Also, heavy ice transformations from the annealed phase VIII occurred on heating from 94 to 290 K in a RT experiment on IBR-2 with the resolution  $t_s = 2 \min [108]$ . A 0.3 g sample (99% D<sub>2</sub>O) was compressed to 2.6 GPa at room temperature, left to equilibrate for one hour, and cooled to 90 K; at the final stage of the experiment, the sample remained under atmospheric pressure. Figure 14 shows consecutive neutron diffraction patterns obtained at each stage. Their analysis demonstrated that the initial high-pressure phase



**Figure 14.** A series of neutron diffraction patterns obtained in course of heavy ice heating from 94 K (the beginning of the time-scale) to 290 K (the end of the time-scale). The wavelength scale (in arbitrary units) corresponds to interplanar distances. The large peak in the beginning of the scale corresponds to the initial phase VIII which turns to amorphous phases *lda* and *hda*; this transition is followed by the appearance of phase *Ic* cubic peaks, the latter phase turns to the hexagonal phase *Ih*.

VIII persisted up to 130 K. Between 130 and 135 K, diffraction peaks corresponding to this phase totally disappeared and were replaced by two broad maxima at  $d \approx 3.65$  A and  $d \approx 3.01$  A with a singularity at  $d \approx 3.85$  A. These values almost exactly corresponded to d values found earlier for the high-density amorphous phase, peak (111) of the cubical ice phase, and the low-density amorphous phase; this suggested the appearance of a mixture of amorphous phases *hda* and *lda* and phase *Ic* nuclei. This state was apparent up to 150-160 K and was followed by the complete transition to the cubic phase *Ic* and then to the hexagonal phase *Ih* (at T = 230 K). Moreover, transition  $Ic \rightarrow Ih$  turned out to be of complex nature in that it started with the peak (100) shaping (i.e. molecular ordering in the basic plane of the hexagonal lattice) followed by reciprocated plane ordering.

Therefore, the above experiment in which diffraction spectra were measured for only 6 hours has revealed a series of new facts including the previously unknown phase transition of ice VIII to amorphous ice *hda*, the likely coexistence of high and low-density amorphous phases (i.e. the *hda*  $\rightarrow$  *lda* transition which, if any, must be a first order one), and complex nature of the hexagonal phase formation.

## 7.3 Ultimate possibilities for studying transient processes with a pulsed neutron source

In the above examples of RT experiments, the measuring time for one neutron diffraction pattern ranged from a few seconds to several minutes, that is the data were collected during 10 or more pulses of the IBR-2 reactor (periodicity 0.2 s). Optimisation of experimental conditions allowed necessary statistics to be obtained within a single power pulse which confirms results of a model experiment [109] presented in Fig. 15. Comparison of neutron diffraction patterns shown in Fig. 15 demonstrates perfectly well characteristic features of the diffraction picture notwithstanding poor statistical accuracy of measuring the spectrum from a single power pulse of the reactor. In a similar LANSCE experiment [110], the Bragg jumps have been recorded in the emission spectrum of polycrystal iron during a single pulse from the reactor. These data indicate that the time-resolution of 20-200 ms (periods of repeated pulses from the sources) in studies of irreversible processes is already achievable even if it has until recently seemed altogether impossible in neutron diffraction. However, whenever necessary statistics can be obtained from a single pulse, there is also a possibility to go further (in scattering geometry) by means of the method proposed in



**Figure 15.** Neutron diffraction patterns from a polycrystal molibdenum sample measured at IBR-2 for 0.2 s (one source pulse) (a) and 1 min (300 source pulses) (b).

Ref. [109]. According to the Bragg equation, the diffraction peak must undergo a  $\Delta \lambda = 2d \cos \theta \Delta \theta$  wavelength shift if the scattering angle is changed by  $\Delta \theta$ ; for the DN-2 diffractometer at IBR-2, this is equivalent to the time shift by  $\Delta t = 17.8\Delta\theta$  ms at d = 2 A and  $2\theta = 90^{\circ}$ . Therefore, several detectors placed in the region of scattering angles  $90^{\circ}$  with a  $\Delta \theta \approx 3^{\circ}$  shift will record the same diffraction peak with a time shift of  $\Delta t \approx 1$  ms.

The quantity  $\Delta t \approx 1$  ms appears to be close to the limiting time-resolution in neutron diffraction of irreversible processes at pulsed neutron sources. It is comparable with quantities obtained using superbright synchrotron radiation sources but much lower than limiting values available with steady state reactors. Hopefully, the resolution of the order 0.1 s can be achieved with a 150 MW reactor, but current projects of reactors with the power of 100 MW and even 300 MW will hardly be implemented in the near future.

# 8. Studies on transient processes in external fields

Even early IBR-2 neutronographic studies [12, 13] placed special emphasis on the sample irradiation by pulsed neutron beams because it enables an external impact on the sample to be synchronised in the pulsed regime with source pulses. Depending on the pulse duration of a magnetic or electric field and synchronisation conditions, it is possible to observe its effects on the entire spectrum, a few diffraction peaks or a single peak. Pulsed nature of an impact makes it possible to significantly enhance its amplitude and obtain field values unavailable in the steady state regime. The time-resolution in such experiments shows strong dependence on process reversibility (irreversibility) and also on the parameters of the source and the design of the experiment.

Experimental constraints for irreversible processes have been considered in the previous section. Given a specific pulsed source, the reversible processes can be arbitrarily categorised into 'slow', 'fast', and 'very fast', the rate measures being periodicity of source pulses and certain parameters of diffractometers. The following Sections are concerned with two possible modes of designing experiments intended to study reversible transient processes. By way of illustration, they present results of investigations into electric field effects on a ferroelectric NaNO<sub>2</sub> and the influence of a magnetic field with the large amplitude on selected magnetic crystals.

## **8.1** Studies of 'slow' reversible transient processes in the electric field

If the time constant of a process of interest is higher than the frequency of repeated pulses from the source, it is possible to organise an experiment according to the scheme in Fig. 16. The specimen is synchronously affected by a power pulse from the source and an electric field sufficient to induce polarisation. In studies on ferroelectric crystals, electric field voltage depends on the sample coercive field and does not normally exceed several kV cm<sup>-1</sup>. Diffraction spectra from consecutive source pulses are analysed by the time-of-flight technique and stored in different parts of memory. The number of such independent parts N is inferred from the condition  $NT \ge \tau$ , where T is the period of repeated source pulses and  $\tau$  is the characteristic time of the process. After all the parts are filled up, the initial state of the sample is restored, and the process is repeated as many times as is necessary to obtain statistics. Evidently, the time-resolution in this case is equal to the period T, and the curve of a sample parameter vs time has N points. In other words, for a source with T = 10 ms (v = 100 Hz), the processes with  $\tau \ge 50$  ms may be regarded as 'slow' ones.

This scheme was used in an early experiment to observe the polarisation reversal of a NaNO<sub>2</sub> ferroelectric crystal by an electric field [111]. These crystals are known to occur in the



Figure 16. Time-diagram of neutron pulses from the source (a), electric field pulses (b), and diffraction spectra (c) obtained by measuring a process with the time constant higher than the source pulse period.

ferrophase at temperatures below 164 °C while NO2 radicals are in the (100) plane with dipole moments parallel to the [010] axis. If crystal polarisation reversal is induced by a field applied parallel to the [010] axis, rotation of NO<sub>2</sub> groups around either the [001] or [100] axis may be expected. Both possibilities have been discussed in the literature. A diffraction experiment on the pulsed neutron source at the Tohoku University, Japan, with the pulse repetition frequency of 100 Hz, provided the correct model of the process. The results of the experiment are presented in Fig. 17 showing that the intensities of (h00) reflections from the NaNO<sub>2</sub> single crystal change with time whereas the intensities of (001) peaks remain unaltered. A simple calculation of crystal structure factors indicates that this picture is in excellent agreement with a gradual revolution of NO2 groups around the direction [001] for about 40 ms.



**Figure 17.** Time-dependence of integrated intensities of certain diffraction peaks in polarisation reversal of NaNO<sub>2</sub> crystals by an electric field. Peak intensities (200) and (400) undergo marked changes with time whereas peak (002) intensity remains unaltered. This confirms the hypothesis of the rotation of NO<sub>2</sub> groups around the [001] axis during polarisation reversal of the crystal.

## 8.2 Studies of 'fast' and 'very fast' reversible transient processes

The success of the experiment described in the previous section was largely due to a relatively short period of repeated source pulses (10 ms) which facilitated the simple design of the study. Similar processes can be examined using sources with pulse periodicity in excess of  $\tau$  even though the scheme of experiments should be somewhat modified compared with that in Fig. 16. A field pulse is fed onto the crystal with a certain delay  $T_0$  relative to a source pulse, and the diffraction patterns are recorded. In the end of the period of repeated source pulses, a field pulse is applied to the crystal to restore its initial state; after this, the process is repeated as many times as is necessary to collect statistics. A measurement made with a fixed delay of a field pulse versus a neutron source pulse corresponds to finding one experimental point for the timedependence of a crystal parameter. Measurements at different  $T_0$  are necessary to obtain the entire curve.

As compared with the measuring scheme for 'slow' processes, sample polarisation reversal in this method occurs in the time-interval between source pulses; moreover, there are higher demands of the front slope for field pulses: they must be smaller and match the width of a neutron pulse from the source. It is the pulse width that restricts from below the achievable time-resolution in an experiment organised in compliance with this scheme. In other words, characteristic times of the processes being studied (i.e. 'fast' processes) can be less than 1 ms.

Even faster transient processes can be examined if the analysis concerns changes in the shape of diffraction peaks following the application of an external field to the crystal rather than changes in their total intensity as in the two previous approaches. In this case, the time-resolution  $\Delta t$  is limited by uncertainties related to the field size at a given moment and angular uncertainties during neutron diffraction on a single crystal [112]:

$$\Delta t = cL_2 \left[ \left( \frac{cL_1}{\tau_s} \right)^2 + \left( \frac{\tan \theta}{\lambda \Delta \theta} \right)^2 \right]^{-1/2}, \tag{41}$$

where c = 252.778 is the constant for the conversion of A to µs if distances are measured in m,  $L_1$  and  $L_2$  are the flight paths from the source to the sample or between the sample and the detector,  $\tau_s$  is the source pulse width,  $\Delta\theta$  are the angular uncertainties caused by collimation of the primary beam and the sample mosaic,  $\theta$  and  $\lambda$  are the Bragg angle and the wavelength respectively at which the diffraction peak is measured. Under experimental conditions realised on the SNIM spectrometer at IBR-2 [113] in a single crystal study in strong pulsed magnetic fields, the authors achieved the time-resolution of the order 2–4 µs.

A magnetic field pulse in SNIM has the form of a  $500-2000 \mu$ s wide sinusoid segment with the amplitude of up to 200 kOe. To achieve this, an electric pulse with the amplitude of up to 50 kA (150 kA being the limiting value) is fed onto a special pulse magnet. Another currently operated pulse magnetic device at the KENS source (Japan) [114] provides similar possibilities in terms of the magnetic field amplitude but is inferior to SNIM as far as the intensity is concerned because of the lower pulse power of the source and higher repeated pulse frequency.

The recent SNIM studies of magnetic crystal phenomena induced by a strong external pulsed field include hysteresis of a spin-flop transition in  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> [115], spin-flop transition kinetics in Cr<sub>2</sub>O<sub>3</sub> [116], induced weak antiferromagnetism in YFeO<sub>3</sub> and HoFeO<sub>3</sub> [117, 118], etc.

In a kinetics study of the reorientation spin-flop transition in rhombohedral  $Cr_2O_3$  single crystals, they were subjected to the effect of a field with the amplitude of up to 150 kOe for 1 ms. The altered orientation of atomic magnetic moments was evaluated based on the field-induced relative changes in the diffraction peak intensity (Fig. 18). An important unexpected result of this study was the coherent nature of the moment reorientation throughout the sample volume (ca. 1 cm<sup>3</sup>). This observation is in conflict with the generally accepted concept of the kinetics of the first-order phase transition via the nucleation of a new phase. Evidently, new models need to be developed and numerical calculations made for such cases.

### 9. Internal mechanical stress studies

Heating and mechanical impacts inherent in industrial production manufacturing may be responsible for mechan-



**Figure 18.** Resultant spectrum (initial peak intensity minus peak intensity following field application) from plane (224) of a  $Cr_2O_3$  single crystal at T = 130 K. Upper points show changes of the magnetic field at the sample. Its amplitude is 78.8 kOe.

ical stress in the materials which is known to affect the strength of constructions; specifically, they are able to promote cracking. Also, residual stress is likely to develop as a result of deformation when some parts of the article undergo plastic deformation while others are subject to elastic strain [119, 120]. Such stress may arise in macroscopic regions, i.e. permanent pipe bends where the subsurface and inner layers undergo plastic and elastic strains respectively.

Of special interest for engineers are non-destructive methods of monitoring the behaviour of materials, constructions, and their units under effect of external factors. Various physical methods are used in the non-destructive control of internal stress, viz. X-ray diffraction, ultrasonic studies, magnetic measurements, etc. [121]. Recently, there has been increasing interest in the use of the neutron diffraction technique although it is for the time being largely employed for calibration and certain specific purposes including, in the first place, the identification of internal stress deep in the construction volume (neutrons are able to penetrate to the depth of 4 cm in steel and 10 cm in aluminium) and the analysis of multiphase materials (composites, ceramics, alloys, reinforced materials) where neutron diffraction can provide information about stress distribution in individual components. Moreover, this technique allows the product microstructure to be most thoroughly investigated. Indeed, diffraction peak displacements are used to evaluate the magnitude of deformation and estimate microstress. Analysis of peak spreading reveals the so-called third-order strains interconnected via microstresses in crystal grains. Finally, peak intensity data may be used to analyse the distribution of crystal orientations (product texture).

The use of neutron diffractometry for the analysis of internal mechanical stress dates back to 1981 [122]. Such analysis is possible provided both high-fluxes and highresolution are available since the magnitude of deformation of a crystal lattice (macrostrain)

$$e_{hkl} = \frac{d_{hkl} - d_{0hkl}}{d_{0hkl}} , \qquad (42)$$

where  $d_{hkl}$  and  $d_{0hkl}$  (interplanar distances for distorted and intact lattices respectively) are normally of the order  $10^{-3}$ –  $10^{-4}$ . That is why such studies became feasible no sooner than high-resolution power diffractometers had been developed. The majority of experiments are presently carried out with double-axis diffractometers, but the experience of exploiting diffractometers on high-flux short-pulsed sources [123–125] and Fourier diffractometers [126–128] indicates that the time-of-flight technique has many important advantages if applied to internal stress studies. To begin with, its offers the possibility to work in fixed geometry and measure several diffraction peaks simultaneously. Scattering geometry within an angular range of  $\pm 90^{\circ}$  proved to be especially convenient because it separates in the best way a certain scattering volume and allows for parallel stress measurements in two directions.

In the general case, deformation and stress have six components and are represented as tensors. Axes 0xyz inside a sample and strain tensor  $\varepsilon$  at a point in this coordinate system being known, the deformation measured along the vector with directive cosines (*lmn*) relative to 0xyz is defined by the following relation [129]:

$$e(lmn) = l^{2}\varepsilon_{xx} + m^{2}\varepsilon_{yy} + n^{2}\varepsilon_{yy} + 2lm\varepsilon_{xy} + 2mn\varepsilon_{yz} + 2nl\varepsilon_{xz} .$$
(43)

At least 6 measures of e(lmn) are needed to determine all tensor  $\varepsilon$  components, and the accuracy grows as the number of measurements increases. Given  $\varepsilon$ , it is possible to find main axes and major strains  $\varepsilon^d$  by means of diagonalisation. In the framework of an elastic isotropic model, major internal stresses are related to the macroscopic Young modulus *E* and the Poisson relation v by the expression

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$$\begin{bmatrix} \sigma_{x} & & \\ & \sigma_{y} & \\ & & \sigma_{z} \end{bmatrix} = \frac{E}{1+\nu} \begin{bmatrix} e_{x^{d}} & & \\ & e_{y^{d}} & \\ & & e_{z^{d}} \end{bmatrix} + \frac{\nu E}{(1-2\nu)(1+\nu)} (e_{x^{d}} + e_{y^{d}} + e_{z^{d}}) \begin{bmatrix} 1 & & \\ & 1 & \\ & & 1 \end{bmatrix}.$$
(44)

The assumption of elastic isotropy is used in many situations, but it should be considered as a first approximation. In the general case, both Young moduli and Poisson relations in Eqn (44) depend on the Miller indices; this reflects crystal anisotropy. Taking the texture into account when estimating stress in polycrystals is rather a difficult task. In the elastic region, it is possible to use models [129, 130] in which either strain or stress is considered to be continuous during the passage across the grain boundary or a more realistic model [131] which in part takes into account face interactions. Today, there is no complete theory of stress development at the level of intercrystal interaction in the elastic-plastic domain, but it is worth mentioning an interesting approach based on the application of gauge theories to elastic media [132].

Let us consider results of a study on austenitic steel pipes with a welded ferritic coat [133]. Such antirust coating effectively protects pipes even in chemically active media. However, further development of this technique is somewhat hampered by rather intricate distribution patterns of residual stress unamenable to control. Therefore, it is crucial to analyse internal stress along the interface between the steel and the ferritic layer. Mechanical measurement of deformation during gradual grinding of the sample has until recently been the most widely used method of such analysis. However, non-destructive neutron diffractometry appears to be a more informative and useful tool for the optimisation of the technology.

The sample was a pipe of austenitic steel ( $\gamma$ -phase) with the 15 mm thick walls and the internal radius of 148 mm coated with 7 layers of ferritic steel ( $\alpha$ -phase) of the 2NiMo 1VP type having 135 welds along the full length of 1100 mm. The pipe segment selected for the study is shown in Fig. 19.



**Figure 19.** A sample cut out of a pipe with a welded ferritic layer. The figure shows the diaphragms that close the apertures for incoming and scattered beam. Distances are given in mm.

The experiments were carried out using the HRFD/IBR-2 assembly with two 90° detectors that provided the resolution of 0.4-0.5%. Such a geometry allowed the linear and lateral strain components to be simultaneously measured. Diaphragms at the outlet of the neutron-guide and in front of the detectors were used to set the scanning volumes of  $2.1 \times 4.5 \times 19.4$  and  $2.1 \times 2.6 \times 19.4$  mm<sup>3</sup> for the first and second detectors respectively. Measurements far from the transition layer revealed pronounced texture in the  $\gamma$ -phase (the intensity of one of the Bragg peaks was approximately 8 times that of the calculated value for randomly oriented crystallites). No apparent texture was found in the  $\alpha$ -phase.

Axes x, y, z shown in Fig. 19 are supposed to be the main axes of the stress tensor for the described sample. Then, in the elastic medium model, stress tensor components are possible to infer from Eqn (44). The axial components were not measured in this experiment; therefore, the difference

$$\sigma_{\rm t} - \sigma_{\rm r} = \frac{E}{1+\mu} (\varepsilon_{\rm t} - \varepsilon_{\rm r}) \tag{45}$$

was calculated, where t, r are the tangential and radial directions of the vector respectively. Figure 20 shows that this difference depends on the distance from the centre of a weld. It also represents results of mechanical or destructive monitoring (solid line). On the whole, the figure demonstrates good qualitative agreement between the data. The discrepancy in the  $\gamma$ -phase can be explained by the necessity to take into account the texture in diffraction data processing.



**Figure 20.** The difference between the tangential and radial internal stress components in the pipe shown in Fig. 19 measured in a diffraction experiment  $(\Box, \bigcirc)$  and obtained by the destructive control technique (dashed line).

To summarise, time-of-flight diffractometry provides an ample opportunity for the analysis of composite industrial products, and its further improvement is promising in terms of the development of non-destructive methods of control. At the same time, many technical problems remain to be solved, e.g. determination of interplanar distances in an intact lattice (which is always distorted in real materials), accounting for non-linear effects in the stress vs orientation relationship, taking into account the texture, etc. In a word, neutron diffractometry as a non-destructive tool for quality control of industrial products deserves more attention of physicists.

### 10. Conclusion

In conclusion, there are some most important distinctive features of time-of-flight diffractometry:

(1) fixed scattering geometry which allows for the installation of additional devices at the sample site (cryostats, furnaces, pressure chambers, magnets) for experimenting under variable external conditions;

(2) parallel data accumulation in a sector or volume of the crystal's reciprocal space necessary, for instance, in the analysis of incommensurably modulated structures and diffuse scattering associated with defects in the crystal structure;

(3) greater opportunities to reach higher resolution and especially higher intensity than those available with doubleaxis diffractometers;

(4) pulsed neutron bombardment of the sample accounting for a more effective use of external pulsed fields.

These features of time-of-flight diffractometry allow for the experimentation with various samples and under variable environmental conditions. Major problems amenable to solution by this technique are listed in Table 5 and highlighted in part in the present review. This classification is arbitrary and reflects the current situation 'averaged' over potentialities of modern diffractometers.

**Table 5.** Major problems solved by the neutron diffraction technique with the use of double-axis and time-of-flight diffractometers (+ the problem is possible to solve, ++ the method offers certain advantages, ++ + a very promising method)

Problem\Diffractometer	Double-axis	Time-of-flight
Structural analysis of single crystals	+++	++
Ab initio structure determination	++	+ + +
Structural analysis of biocrystals	++	+ + +
Structure modulation	+	+ + +
Disordered structures	++	+ + +
Polycrystal cell autoindexation	+	++
Polycrystal structure determination	++	+ + +
High pressure	+	+ + +
Phase transition	++	+ + +
Magnetic structures	+ + +	++
Microsamples (0.1 mm <sup>3</sup> )	+ + +	++
Phase analysis of composition	++	+ + +
Fluids and amorphous matter	+	+ + +
Internal stress	++	+ + +
Texture	+	+ + +
Irreversible transient processes	++	+ + +
Reversible transient processes in fields	+	+++

Time-of-flight diffractometry has recently become a valuable tool for structural studies in physics of condensed media, biology, chemistry, and the science of materials. The potential of time-of-flight diffractometers for experimenting on both mono- and polycrystals is much greater than that of double-axis diffractometers at steady state neutron sources. It is sure to increase as new high-flux pulsed neutron sources are constructed.

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