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Original Paper

The birth of time-of-flight (TOF) neutron powder diffraction at pulsed neutron source (invited)

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Behind every improvement there is a story.
The early history of the TOF neutron powder diffraction technique is presented. Successes and problems in the application of this technique in material science are reported. Powder diffraction technique is very useful when materials, in a single crystal form, reveal complicated electric and magnetic domain structures. Finding and describing the magnetic structure of multiferroics is the great success of ultra-high resolution TOF neutron diffraction. This unique role of the TOF method in discovery of the modulated magnetic structure of $BiFeO_3$ is presented. To date, the TOF powder neutron diffraction technique gives the richest information on the long period modulated magnetic structure of $BiFeO_3$ and its solid solutions. Determination of magnetic moment direction in a crystal lattice is the unique area of application of the TOF technique. The current status and perspectives of the application of the TOF neutron powder diffraction technique in material science are presented in the review.

1 Introduction to the TOF method

The idea of the application of the TOF technique to neutron diffraction was first discussed in the year 1956 by R. D. Lowde [1], in the year 1957 by G. R. Ringo [2], in and later in the year 1960 by P. A. Egelstaff [3]. The merit of this idea was to collect, at a constant angle, a white beam neutron spectrum diffracted on a polycrystalline sample. Therefore, it was proposed to use Braggs's law differently as it is done in neutron diffraction in the standard Debye-Scherrer method [4, 5].

After fifty years of improvements, the TOF neutron powder diffraction technique is nowadays one of the standard techniques used for crystal and magnetic structure determination of polycrystalline materials at pulsed neutron sources. Nevertheless the beginnings of the TOF method at a pulsed neutron source are poorly described in the literature.

Powder neutron diffraction is a very useful technique for crystal structure determination because many materials (e.g. perovskite-like materials) reveal complicated electric and magnetic domain structures when they appear in a single crystal form. Polycrystalline materials usually do not show domains. The utility of neutrons as a crystallographic probe is a direct consequence of the relative weakness of the fundamental neutron-matter interactions. The compatibility of slow neutron wavelengths with inter-atomic distances permitted the performance of diffraction studies of materials similar to X-ray diffraction studies. As a neutron possesses a magnetic moment, the magnetic structure of matter can also be determined using so called magnetic neutron diffraction. This review is limited only to the investigation of elastic slow neutron scattering in polycrystalline materials using the TOF method at pulsed neutron sources. Specifically, such unique materials as multiferroics and their studies will be described.

TOF diffractometers operate differently than reactor constant wavelength (CW) diffractometers based on the standard Debye-Scherrer method. For neutrons, the Debye-Scherrer method was first developed and used in the 1940's [4, 5]. Instead of measuring Bragg reflection by scanning a detector from low to high 2θ scattering angles, in the TOF technique a neutron spectrum of scattered neutrons is measured at a constant scattering angle, $2\theta_o$.

In the TOF experiments, the neutron beam coming from a moderator is polychromatic, and for neutrons

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scattered at a fixed scattering angle, $2\theta_0$, on polycrystal, one can express Bragg's law as:

$$\lambda_{hkl} = 2d_{hkl}\sin\theta_0 \quad (1)$$

where λ_{hkl} is the neutron wavelength and d_{hkl} the interplanar distance in the crystal.

The neutron wavelength is determined, according to the de Broglie relation, by the neutron momentum, mV as:

$$\lambda = {}^{h}/_{mV} = ht/ml = At \quad (2)$$

Where h is the Planck constant, V neutron velocity, m neutron mass, l a flight path, A constant and t time of flight.

In 1963, the newly proposed TOF method [1–3] was tested in structural studies of polycrystals using two different experimental setups.

The first one was a steady state reactor-based TOF diffractometer using Fermi choppers to form neutron pulses out of thermal neutron white beams coming from the reactor's channel. The first steady-state reactor-based experiment where the TOF method was tested was done in 1963 in Świerk, Poland [6]. Soon, similar tests on polycrystalline materials using the TOF method at steady state reactors have been undertaken e.g. in the USA [7, 8]. The best resolution TOF diffractometer based on the use of a steady-state reactor neutron spectrum, was the TOF diffractometer constructed in Garching, Germany in 1973 [9]. In 1980, the Garching diffractometer was used in the discovery of the magnetic cycloid in $BiFeO_3$ using the TOF method [10].

In 1963 the first TOF diffractometer, at a pulsed neutron source was built at the Dubna pulsed reactor IBR [11]. It was the second setup of a TOF diffractometer, in which the fast neutron pulses were created, via nuclear reactions. Almost all findings and improvements of the early TOF method (1963–65) were presented in the few reports of the Joint Institute of Nuclear Research in Dubna [12] and in details are described in my Ph. D. thesis [13]. The first publication in which the pulsed neutron source was applied in structure analysis of known materials was published in 1963 [11]. It was the first piece of evidence that the TOF method idea works properly. In the fast neutron pulse, produced by nuclear reactions, neutron possess energy of the order of MeV. These neutron pulses have to be moderated. A neutron deposits its MeV energy and becomes "slow" having an energy of E ≈ meV at the end of the process. This process is very complicated. Special study how slow neutron pulses are formed in this process was described in [14]. The important parameter of the pulsed neutron source is its duty cycle, e.g. the number of neutron bursts per second. It limits the flight path and hence the instrument length without pulse overlapping of neutrons from different bursts. Electron accelerators were also used to get neutron pulses and do diffraction studies (see e.g. [15, 16]). This setup is used at all spallation sources at present.

The resolution of a diffractometer, $\Delta d/d$, is a measure of the spread in the Bragg reflection for a given d-spacing and is of great importance in determining the overall quality of a diffractometer. On a pulsed source, the resolution has three major contributions: a timing uncertainty, Δt; an angular uncertainty, $\Delta\theta$, and flight path uncertainties, Δl.

The overall performance of a TOF diffractometer depends on its resolution and intensity. The resolution of a TOF diffractometer is described by (see e.g. [17]):

$$\frac{\Delta d}{d} = \left[\left(\frac{\Delta t}{t}\right)^2 + (\Delta\theta\cot\theta)^2 + \left(\frac{\Delta l}{l}\right)^2\right]^{1/2} \quad (3)$$

where Δd, Δt, Δl and $\Delta\theta$ are respectively the uncertainties of the lattice spacing, d, the flight time, t, for the neutron over the total flight path, l, and the Bragg angle, θ. Since path uncertainties and angular uncertainties are independent of wavelength, the overall geometrical contribution to resolution is nominally constant when the scattering angle is fixed. The main contribution to Δt gives the moderation process of neutrons.

Using the TOF method it is possible to reach very high resolution in the diffraction of polycrystalline materials. Such an ultra high resolution TOF diffractometer was constructed at the Garching steady-state reactor 'Atom Ei' with the long flight path $l \approx 150$ m and with a detector bank in a back scattering configuration ($2\theta = 178^0$). It reached very high resolution of $\Delta d/d \approx 8 \times 10^{-4}$. A curved neutron guide tube along the incident flight path substantially increased the incident flux on the sample. This diffractometer, possessed the best resolution in the world to date [9]. It was used in the first observation and determination of a modulated magnetic structure in multiferroic perovskite $BiFeO_3$ [10] This diffractometer reached the best resolution, but its intensity was more than two orders of magnitude lower than the HRPD diffractometer at the ISIS spallation source [17]. Nowadays, HRPD is the best resolution neutron diffractometer in the world and is designed to achieve an optimal balance between the maximum practical resolution attainable $\Delta d/d = 4\text{–}5 \times 10^{-4}$ [17] and reasonable counting times.

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Neutron intensity is the second important parameter of each TOF diffractometer. The formula for intensity of the *(hkl)* diffraction maximum in the TOF method was first presented in [18] with $A(\lambda)$ absorption correction added [12, 13]:

$$I_{hkl} = \frac{\left[i(\lambda)\lambda^4 |F|^2 \, jA(\lambda)\right]_{hkl}}{4 \sin\theta_0} \frac{\delta V}{V^2} ctg\theta_0 \Delta\theta_0 \qquad (4)$$

where F is the structure factor, j the multiplicity factor, $i(\lambda)$ the neutron intensity, λ the neutron wavelength, V, and δV the volumes of the unit cell and the crystal respectively, θ the scattering angle and $A(\lambda)$ the absorption correction. In the Eq. (4) the intensity of diffracted neutrons is proportional to λ^4. This is a consequence of a replacing in the Debye-Scherrer diffraction formula $\lambda_0 = const$ by $\theta_0 = const$ and do integration of the formula within the acceptance angle $\Delta\theta_0$ of the detector.

It was found that absorption in the sample may be wavelength dependent, and we introduced an additional term, $A(\lambda)$, to the above Eq. (4). The determination of absorption correction $A(\lambda)$ and its wavelength dependence is described in [12, 13]. The introduction of experimentally determined absorption corrections into calculations of structure parameters of tungsten reduce the reliability factor R by fifty percent [12, 13].

The intensity of diffracted neutrons for the *(hkl)* reflection depends on the neutron intensity $i(\lambda)$ in neutron spectrum and on the factor λ^4, which creates together with the primary spectrum $i(\lambda)$ the so called neutron effective spectrum $i(\lambda)\lambda^4$.

2 The realization of the TOF diffraction idea at the first pulsed neutron source: the IBR reactor

Fifty years ago, the TOF method was elaborated for the first pulsed neutron source [19] placed in the Joint Institute of Nuclear Research in Dubna, Russia. The IBR pulsed reactor was constructed for nuclear physics research. Investigation on slow neutron diffraction was also discussed. The IBR pulsed reactor was only a 1 kW neutron pulse source. The person who guided these studies in Dubna was F. L. Shapiro, the Vice Director of the Neutron Laboratory of the Joint Institute of Nuclear Research. The flux of the IBR was too low to use the standard Debye-Scherrer method and do conventional neutron diffraction. To develop structure and phonon dispersion relation studies at the IBR, one had to use non-conventional techniques. After many discussions with B. Buras, who was, at that time the head of the Solid State Physics Department at the Institute of Nuclear Research and the head of the Neutron Laboratory at the University of Warsaw, they (BB and FLS) both decided to start common diffraction studies using the TOF method at the pulsed reactor. It was just the right moment to do so. Fig. 1 shows photos of B. Buras and F. L. Shapiro, the two initiators of the application of the TOF method in neutron diffraction studies.

Fig. 1 The two initiators of the application of the TOF neutron diffraction method to studies of crystal structure of polycrystalline materials: (a) Bronisław Buras (1915–1994) and (b) Fiodor Lvovitch Shapiro (1915–1973).

The idea of applying the TOF method to solid state physics, as was mentioned in the Introduction, was already published, [1–3].

In 1963 was started a construction of a TOF diffractometer at the IBR reactor. This was the first such diffractometer at a pulsed neutron source. In front of me stood the IBR reactor wall with a shutter closing channel number four. Around me, there were blocks made out of concrete (our future shielding). TOF diffraction at a pulsed source at the beginning of 1963 looked rather sad and hopeless. My role in this enterprise was rather trivial. Having two supervisors (see Fig. 1), I had rather vague prospects to complete my Ph. D. thesis having only an almost empty reactor hall.

The construction and physical principle of the IBR reactor is described in [19], where the role of IBR reactor elements is described. The pulsed fast neutron reactor IBR produced five fast neutron bursts per second due to the movement of two discs, which crossed the reactor active zone simultaneously. The static active zone was made out of plutonium. The discs themselves contained uranium ^{235}U. In order to produce slow neutrons, a moderator was placed in front of the reactor (e.g. [19]). The scheme of the pulsed reactor IBR is shown in Fig. 2.

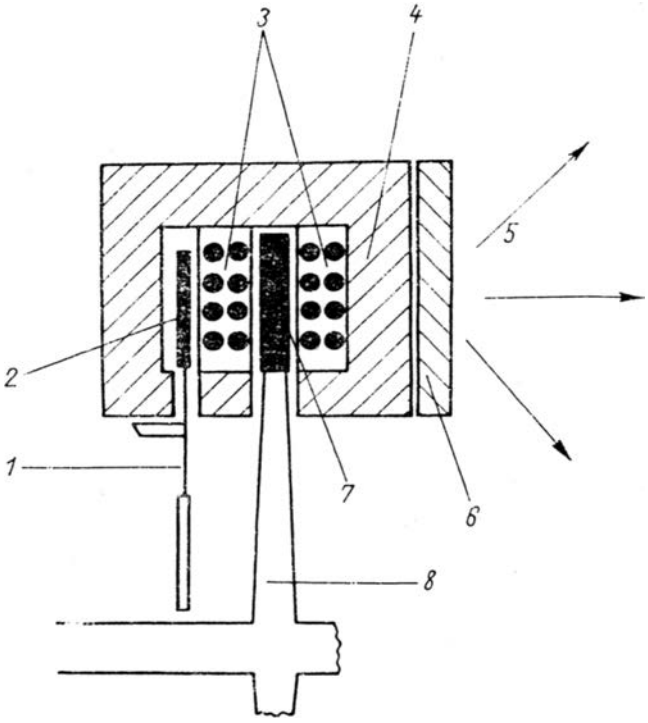

Fig. 2 Scheme of the IBR reactor. Rotating small disc (1) and big disc (8), plutonium active zone (3), reflector (4), neutrons (5), moderator (6), U^{235} main moving part (7) and (2) U^{235} additional moving part (after [19]).

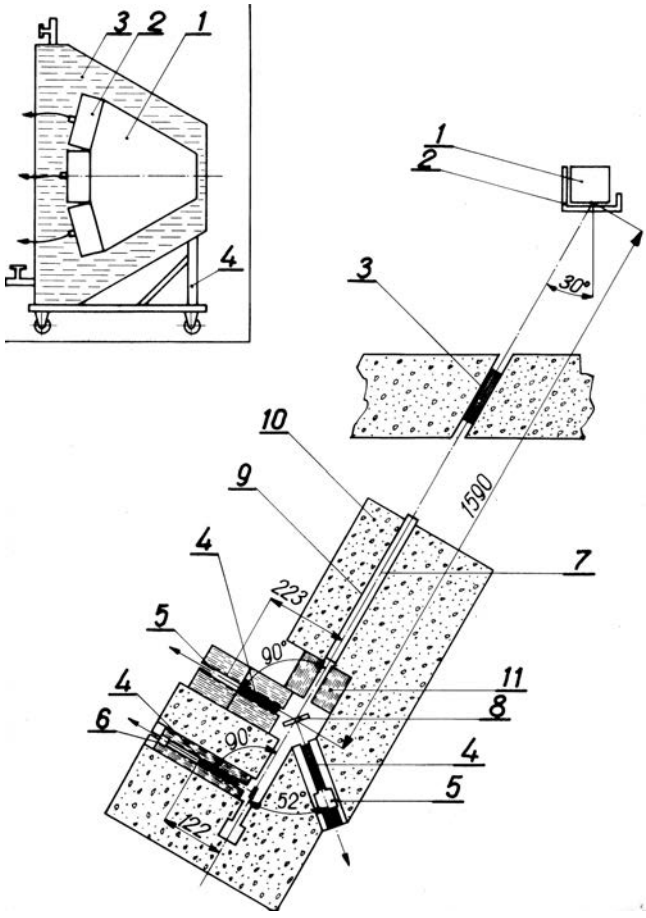

Fig. 3 The TOF diffractometer at the IBR reactor in Dubna with geometrical focusing built in 1964–5 (after [12, 13]). Main figure: 1-reactor core, 2-moderator, 3 and 4-collimators, 5 and 6-scintillation counters, 7 and 9-vacuum tube, 8-sample, 10-concrete shielding, 11-water shielding. Left upper corner: special type collimator to collect neutrons from about 1/6 of the Debye-Scherrer ring: 1-soller collimator, 2-scintillation counters, 3-water shielding, 4-base.

The first neutron diffraction pattern using a pulsed neutron source (IBR) was collected at channel number 4 and the diffraction results were published [11]. Even using a source with a power of 1 kW, it is possible to do neutron diffraction studies. In addition it was evident that the TOF method can be realized at this reactor to investigate the structure of polycrystals. This was a result of our experiments in 1963 [11].

In 1964, it was decided that channel number four of IBR which we had used was needed for another experiment. As a consequence, our TOF diffractometer had to be moved to channel number five of the IBR reactor. Nevertheless, we were very astonished when we found that the resolution of our diffractometer placed on channel number five was much better than on the previous one. This was a great improvement. F.L. Shapiro, by chance, realized geometrical focusing. Therefore, F.L. Shapiro is the first discoverer of the **focusing effect** in TOF diffraction. The discovery of the focusing effect in TOF diffraction and the role of F.L. Shapiro were totally forgotten. Nowadays, the geometrical focusing effect is widely applied in all TOF diffractometers at spallation neutron sources (e.g. [17]).

The final design of the TOF spectrometer at the IBR reactor was described in [12, 13] and presented at the International Congress of Crystallography in Moscow, 1966 [20]. The TOF diffractometer using channel five of the IBR reactor is shown in Fig. 3.

In pulsed sources, the most effective moderators are hydrogenous materials, which can be tailored favouring either high resolution (short moderation times) or high intensity. At the IBR reactor, we finally used a flat, 4 cm water poisoned moderator. We did systematic studies of the influence of poisoning on the resolution of a diffractometer. When a fast neutron pulse is slowed down in a moderator, the characteristic shape of the fast neutron pulse is drastically changed. The pulse width is usually dominated by neutron thermalization time, as shown in

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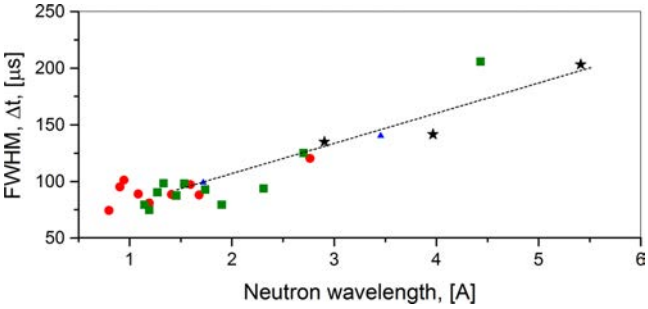

Fig. 4 Full width at half maximum (FWHM), Δt, of the diffraction maxima of different materials, Si and $BiFeO_3$, at scattering angle $2\theta = 90^o$ and 52^o, is shown as a function of neutron wavelength (after [13])

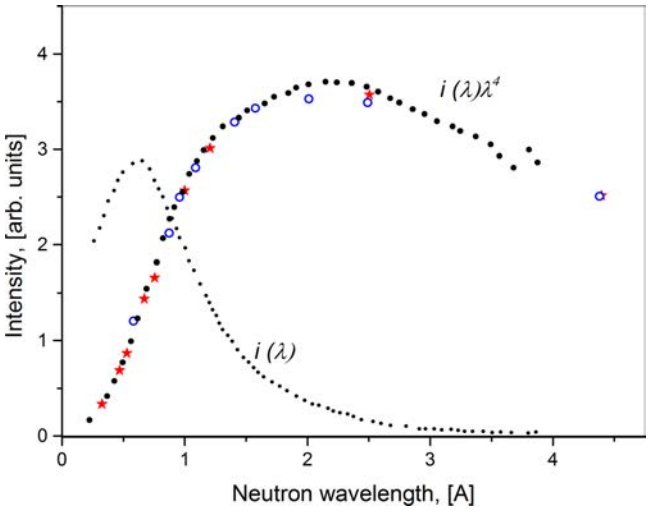

Fig. 5 The spectra of the Dubna IBR reactor: direct neutron spectrum $i(\lambda)$ and effective spectrum $i(\lambda)\lambda^4$ (after [11, 13]).

[12, 13]. For obtaining high resolution results, it was critical to employ the right moderator.

As Δt is roughly proportional to λ (see Fig. 4), the time contribution to the resolution of the Dubna diffractometer (see the Eq. (3), $\Delta t/t = \Delta\lambda/\lambda$, was nominally constant. In Fig 4, the FWHM of diffraction maxima of different materials are shown. The FWHM is linearly dependent on the neutron wavelength, λ. The value of FWHM of 100 μsec at 1 Å was the consequence of the fast neutron burst width of the IBR, which was roughly 90 μsec.

The Carpenter-Ikeda mathematical formula derived in [14], describing the shape of moderated neutrons at a pulsed neutron source, is widely used in the profile analysis of TOF diffraction patterns using the Rietveld code [21].

In the 1960s, we worked on the thermal neutron burst shape, which was not only broad, but also had a tail coming from delayed neutrons leaving a moderator. Doing experimental tests, we found a method to get a shorter pulse of neutrons, outgoing from a moderator, not losing much neutron intensity. It seemed to us that "poisoning" the moderator would be a good method to shorten the pulse in the moderation process. Due to poisoning the moderator, tails of diffraction lines were cut, and the intensity of the silicon diffraction patterns collected using a water moderator poisoned with 0.6 percent of H_3BO_3 dropped only by 30% in respect to diffraction with the pure water moderator. The resolution of the instrument improved [12, 13]. At present, the process of poisoning the moderator is a popular and widely applied method to form the neutron pulse in modern pulsed neutron sources (e.g. [17]).

A neutron pulse shape also depends on the moderator material, its shape and temperature. For long wavelength neutrons, which are important to use for application of ultra-high resolution TOF magnetic diffraction, the process of cooling the moderator appeared to be effective in raising the intensity of neutron flux in this region of the neutron wavelengths. The intensity of slow neutrons rises by a factor of two at T = 77 K when the paraffin moderator was cooled down. The neutron spectra and neutron pulse shape for different moderator forms were measured using TOF diffraction patterns of silicon. The choice of the moderator was dependent on the type of experiment one would like to do. High intensity experiments require a complicated moderator shape.

At the IBR reactor, all reactor channels used the same moderator. Therefore, it was not so easy to reach an agreement between users. Later, I encountered similar problem at spallation source, when the diffractometer used the same moderator as few other channels.

At the IBR reactor, we used neutron detectors with scintillator $ZnS(Ag)+B_2O_3$ enriched with B^{10}. The detectors at scattering angles $2\theta = 90^0$ and $2\theta = 52^0$ had a 300 cm^2 active area, and each of the three sections of a special detector (insert in Fig. 3) at $2\theta = 90^0$ had 500 cm^2 out of a total 1500 cm^2 active area.

The neutron effective spectrum $i(\lambda)\lambda^4$ at the IBR reactor is presented as a function of neutron wavelength in Fig. 5 [12, 13]. The precision of determination of the neutron effective spectrum $i(\lambda)\lambda^4$ is very important, especially for long wavelength neutrons. In this region, the flux of impinging neutrons and the experimental background are of similar intensity. The background itself is even more difficult to measure for long wavelength neutrons. The total

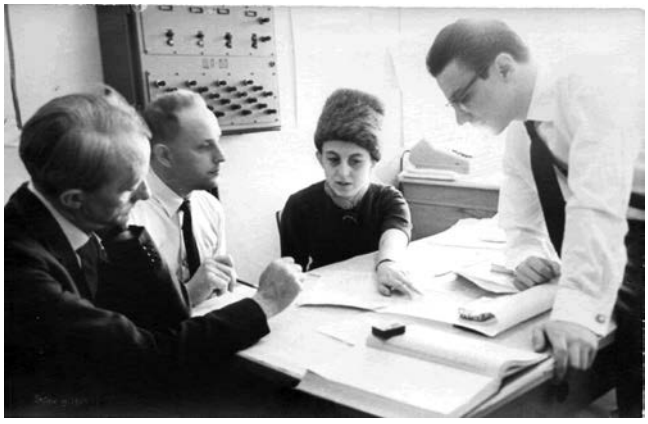

Fig. 6 G. Bacon visit in Dubna in 1965. From left to right: G. Bacon, R.P. Ozerov, I. Sosnowska, J. Sosnowski

accuracy of the TOF structure determination heavily depends on the accuracy of the experimentally determined spectrum $i(\lambda)$.

The intensity of the effective spectrum for long wavelength neutrons at spallation neutron sources makes it possible to observe and measure diffraction maxima even with 10 Å neutrons.

The effective TOF spectrum $i(\lambda)\lambda^4$ of the Dubna IBR reactor presented in Fig. 5 was determined using two alternative methods: diffraction on materials with a known crystal structure and direct beam measurements using the same detector as used later in the diffraction study of unknown structure. Vanadium incoherent scattering may also be used in the determination of a spectrum, but in the long wavelength region, the intensity of incoherent scattering on vanadium is comparable with a neutron experimental background. The neutron spectrum as the difference of these two effects is determined with low accuracy.

The successes and problems in the application early of the TOF diffraction technique for diffraction on polycrystalline materials at the Dubna IBR pulsed reactor and at a steady state reactor in Świerk in material science were summarized in following reviews [13, 22].

At 1965, the Dubna diffractometer was the highest-resolution, $\Delta d/d \approx 10^{-3}$, neutron diffractometer in the world. Prominent crystallographers and physicists visited Dubna in order to analyse and discuss our experiments. Some of them did their own experiments with us. In Fig. 6, such a visit of G. Bacon from Harwell, UK, in 1965 is documented.

After that visit, G. Bacon compared the results of the CW method at Harwell with those of TOF which we got at the IBR reactor, and sent us both diffraction patterns for comparison (see Fig. 7). The Dubna TOF instrument had a better resolution $\Delta d/d = 1\%$ than the standard CW Debye-Scherrer technique ($\lambda = \text{const}$) $\Delta d/d = 5\%$.

3 Spallation neutron sources for TOF neutron diffraction

In the middle of the 1960s, a promising TOF technique was elaborated for a pulse neutron source, but a powerful neutron source itself did not exist. The pulsed reactor IBR and the electron accelerators produced neutron flux that was low. Therefore, a new idea regarding how to get on intense neutron beam was indispensable. Such an idea of getting neutrons by using a spallation reaction of protons of energy GeV on heavy nuclei was presented [23] and prompted many discussions. I was present when G. A. Batolomew described this idea at the IAEA panel in Dubna in the year 1966 [24]. The audience of the IAEA panel of experts was totally sceptical. Their scepticism concerned mostly the flux of a spallation reaction. The early project of the Canadian Neutron Generator was not realized.

Finally, the idea of a neutron spallation source was realized nine years later, as the ZING-P pulsed neutron source, by a team at the Argonne National Laboratory, USA in the year 1975 [25]. A 1 GeV proton accelerator left by high energy physicists was suitable for the spallation neutron source. Later at the ZING-P', the high resolution TOF diffractometer was constructed [26]. In 1981, a dedicated proton accelerator for spallation neutron source was built and a neutron spallation source, IPNS, was commissioned. The Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory can be considered the genesis of all spallation sources dedicated to condensed matter research (see e.g. [27]). At present, the most-modern highest-flux spallation neutron source is (SNS) [28].

4 Certain unique applications of the TOF method

In 1964, the TOF diffraction method at the pulsed reactor IBR was used to solve problems in materials science. In the year 1964 there was a need to find the crystal and magnetic structure of the first multiferroic material, $BiFeO_3$. At that time, nobody knew with what precision (resolution and intensity) one had to do neutron diffraction to solve such a problem. There were already contradictory results from neutron [29] and

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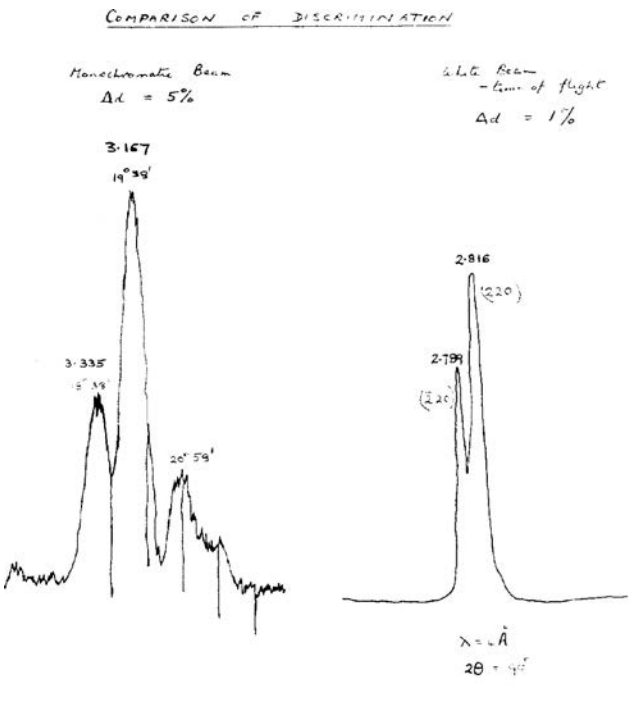

Fig. 7 The comparison of the resolution of the Harwell, UK, CW diffractometer ($\Delta d/d \approx 5\%$) and the Dubna TOF diffractometer ($\Delta d/d \approx 1\%$). Original drawing by G. Bacon, 1965.

electron microscopy. In the 1964, R. P. Ozerov, who was a co-author of the first paper where the magnetic structure of $BiFeO_3$ was determined as the G-antiferromagnetic ordering [30], proposed that I apply the recently developed TOF method at the IBR reactor to investigate the structure of $BiFeO_3$ multiferroics. It began my long lasting story (1964–2014) of the applying the TOF method to investigations of the magneto-electric properties of the $BiFeO_3$ compound and other perovskites oxides. Multiferroic materials have attracted much interest due to the unusual coexistence of ferroelectric and magnetic properties. $BiFeO_3$ is and was one of the most interesting multiferroic material. It is the only known room-temperature multiferroic with $T_C \approx 1100$ K and $T \approx 650$ K, and it exhibits one of the largest spontaneous electric polarisations, $P \approx 80\ \mu C/cm^2$. It has a magnetic cycloid structure with an extremely long period of 62 nm [10], which arises from a competition between the usual symmetric exchange interaction, and the antisymmetric Dzyaloshinskii-Moriya (DM) [31, 32] interaction and the single ion anisotropy [29]. In this section, I will show the role of the TOF neutron diffraction method in determining important structural properties of the bulk $BiFeO_3$.

In 1964, when the TOF diffractometer at a pulsed neutron source was constructed Dzyaloshinskii-Moriya (DM) papers were already published [30, 31]. They described the interaction between a crystal lattice and an ordered magnetic moment. The accuracy of standard neutron diffraction was at that time insufficient to investigate magnetic structure in the lattice with small distortions.

In the 1960's, there was disagreement between an electron diffraction results interpretation which did not show any crystal superstructure in $BiFeO_3$ [29] and Plakhty's CW neutron diffraction studies [29]. Wladimir Plakhty claimed a crystal superstructure exists in $BiFeO_3$. The resolution of the Plakhty's diffractometer was quite coarse, and electron diffraction done by Venievcev's group (for details see the review [34]) with a small single crystal was, for the wide audience, conclusive: a superstructure does not exist. Using the Dubna TOF instrument, we confirmed that a superstructure of the crystal lattice actually exists in the $BiFeO_3$ [35]. It was the **first success** of the high resolution TOF technique to give new information on the unknown crystal structure.

The high resolution of TOF diffraction permitted us also to determine the magnetic moment direction of Fe^{3+} ions in $BiFeO_3$. The high-resolution TOF diffractometer offers the optimal resolution at large interplanar distances, and it is the best tool to analyze the splitting of closely spaced magnetic diffraction lines [10–13] on a neutron diffraction pattern. The very high resolution and the small rhombohedral lattice distortion of the $BiFeO_3$ crystal lattice permitted us to observe the splitting of diffraction peaks, that are observed in CW diffraction as a single one. The neutron diffraction peaks

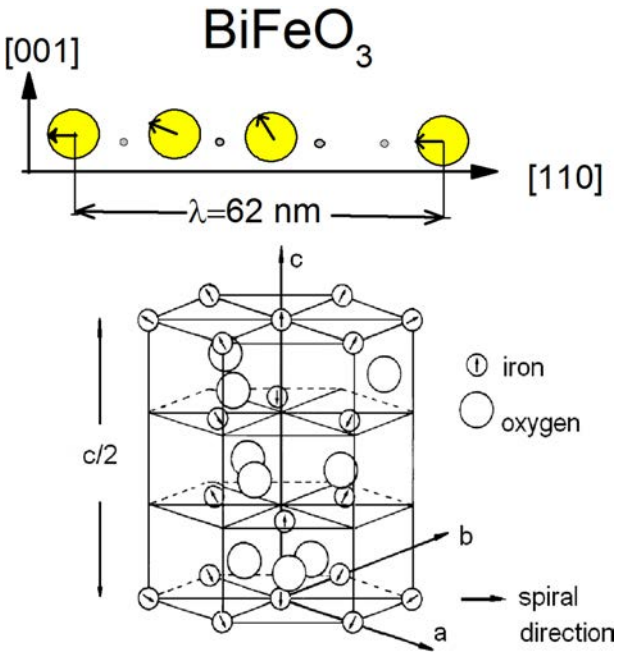

Fig. 8 Portion of the of $BiFeO_3$ lattice with only iron and oxygen ions shown (after [10]). The arrows indicate the Fe^{+3} moment directions of our model. The spiral period ($\lambda = 62.0$ nm). is reduced for illustration purpose (after [10]).

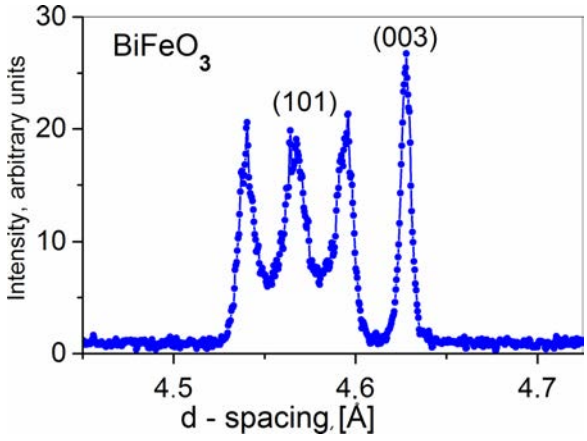

Fig. 9 The high resolution TOF neutron diffraction patterns of polycrystalline $BiFeO_3$ at RT obtained at the HRPD TOF diffractometer, ISIS. The magnetic satellites in the region of the (101) and (003) magnetic reflections are shown (after [36]).

splitting permitted us to determine of the magnetic moment of Fe^{3+} ions and its direction (**the second success** of the TOF method) [35]).

In 1980's we used the high-resolution TOF neutron diffraction in Garching, Germany [10] to investigate magnetic structure of $BiFeO_3$. It was found that the G type antiferromagnetic structure is modified when subjected to a long-range modulation such as is manifested in a cycloidal spiral of the length of $\lambda = 62.0 \pm 2.0$ nm. As was determined, the spiral direction is directed in the [110] direction and the spin rotation plane is (−110) [10] (see Fig. 8).

This finding explains why the linear ME effect was absent in $BiFeO_3$. An alternative explanation of the diffraction experiment was that $BiFeO_3$ has a domain structure possibly so called antiphase domains. These domains might also contribute to such a complicated diffraction pattern that was observed by us in Garching. The presence of the antiphase domains in the sample would give the higher order satellites. Usually, the intensity of the higher order satellite is much smaller than the first one. The low neutron intensity at the Garching TOF diffractometer does not permit us to do such a check. Ten years later, when the HRPD diffractometer at ISIS, UK was constructed [17], we did an experiment where we excluded the possibility of an antiphase domain contribution to the diffraction pattern of $BiFeO_3$ [37] (see also Fig. 9). We could show that the magnetic spiral is very stable and it lasts until the Néel temperature 640 K [36]. Now it is confirmed in [39].

In the year 1994, together with A. Zvezdin, we proposed a Hamiltonian describing a magnetic cycloid found in $BiFeO_3$ including the three main interactions: antisymmetric DM interaction, symmetric exchange interaction and the single ion anisotropy [33]

Many famous and distinguished physicists use the idea of the spiral found in [10] for $BiFeO_3$ and apply it to other perovskites, suggesting that they first discovered long period modulation in antiferromagnets. They copied not only the idea of the long spiral, but also drew the picture of the spiral with an identical direction, plane of rotation etc. They tried to forget the first discovery of the spiral in $BiFeO_3$ [10]. Now we know that spiralling is a common phenomenon. Magnetic spirals appear in almost all multiferroics.

In Table 1, the summaries of the efforts of many groups to confirm the phenomenon of the magnetic cycloid in $BiFeO_3$ are presented.

Indirectly the modulated magnetic ordering in $BiFeO_3$ has been confirmed by nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR) studies. The spiral ordering in $BiFeO_3$ complicates applications of this material in electronic devices. A review on $BiFeO_3$ structural properties has been recently published [41].

Summarizing the TOF neutron diffraction on polycrystalline $BiFeO_3$ has shown that:

Table 1 Magnetic cycloid in $BiFeO_3$ as determined by neutron diffraction, the cycloid direction [110] and the cycloid rotation plane (−110) were confirmed.

Cycloid Length, [nm]	Lattice const. [Å] (in hexagonal setting)	Form	Temperature	Method, instrument, year, reference
62.0 ± 2,	a = 5.779	Poly cryst.	RT	TOF, Garching, 1982, I. [10]
62.0 ± 2.0	a = 5.779	Poly cryst.	RT-600 K	TOF, HRPD, ISIS, 1992, [36]
63.7 ± 2.0	a = 5.581	Poly cryst.	300 K	TOF, HRPD, ISIS, 2006, [37]
63.2 ± 2.0	a = 5.581	Poly cryst.	4 K	TOF, HRPD, ISIS, 2006, [37]
63.7	a = 5.567	Single cryst.	RT	Super 6T2, Saclay, 2008, [38]
66.3 ± 30	a = 5.57	Single cryst.	50 K	TAS, NIST, 2008, [39]
62.0	Monoclinic a = 5.645, b = 5.589, c = 3.95 $\beta = 90.85^0$	Thin layer (110) film –	RT	TAS, NIST and ILL Grenoble, D10 [40]

- in $BiFeO_3$, there exists extremely long period magnetic modulated structure, with the period of 62±2 nm (at RT). This structure is very stable at high and low temperatures,
- the magnetic modulation vector is the directed along the [110] crystallographic direction (R3c group-hexagonal setting),
- the magnetic moment rotation plane is determined by two vectors [111] and [110]. The plane (−110) contains the direction of the spiral and [111] the electric polarization direction.

No other experimental technique is able to give such direct evidence of the modulated magnetic order.

The **third great success** of the application of the TOF method was an observation and determination of a change of the magnetic spiral length with doping. We measured spiral length for $Bi_{1-x}La_xFeO_3$ [42], and we noticed that the spiral length grows with La content. Doping with manganese showed that the spiral period is proportional to the concentration of impurity atoms [43]. However, doping with Co changed the modulated structure to collinear at about 130 K [44]. Nowadays, we know that doping with different atoms is the source of the appearance of some distortion in the modulated magnetic structure of $BiFeO_3$.

5 Summary

Table 2 provides insight the developments of neutron accelerator facilities over time. It compares the peak thermal neutron flux versus the year the facility began or is scheduled to be in operation. Accelerator-based sources show considerable promise for even higher intensities in the future. For comparison, the IBR pulsed reactor power is included.

The only ultra-high resolution TOF diffractometer operated nowadays for long wavelength neutrons (10 Å region) is the HRPD diffractometer at the ISIS spallation source, having the resolution of $\Delta d/d = 4–5\times 10^{-4}$. At new sources, as e.g. SNS, ultra-high resolution diffractometers are planned to be constructed [45]. For shorter wavelength neutrons at all spallation sources, the high resolution was achieved.

Knowledge of the magnetic ground state is very important for applications of multiferroics. Hundreds of papers over the last ten years have shown that the multiferroics, $BiFeO_3$ is a promising candidate for applications, as it is the only one showing these properties at room temperature. As it was shown, ME properties are sensitive to doping and to the form (thin layers, nano crystals etc.) of the sample. Nowadays, we can say that the very unusual cycloid discovered in [10] really exists. The TOF method is unique when we want observe directly magnetic modulation of this structure, which is the fundamental physical parameter deciding if $BiFeO_3$ or its modification may be applied in a technique. Neutron diffraction can be applied for testing multiferroics. Due to the fact that neutrons, having small interactions with matter, neutron diffraction is usually very little influenced by surface effects. This is important for investigations of the bulk properties of multiferroics. This is shown in the latest investigations of the skin effect on the surface of a bulk $BiFeO_3$, which gave misleading information on the bulk properties of the material.

Table 2 A list of pulsed neutron spallation sources.

Facility	Location	Time-average proton beam Power (kW)	Peak flux ($ncm^{-2}s^{-1}$)	Pulsing Frequency (Hz)	Start-up/ Date/Status
IBR	Dubna/pulsed reactor	-	6×10^{13}	5	1960–1968/ Shutdown
ZING-P	Argonne, USA	0.1	5×10^{11}	30	1974–75/Shutdown
ZING-P'	Argonne, USA	3	8×10^{13}	30	1977–80/Shutdown
KENS	KEK, Japan	3.5		20	1980–2006/Shutdown
IPNS	Argonne, USA	7.0	5×10^{15}	30	1981–2008/Shutdown
ISIS	Rutherford-Appleton Lab, UK	190	8×10^{15}	50	1985/Operating
ISIS-TS2		40	-	10	2009/Operating
MLNSC	Los Alamos, USA	60	-	20	2006/Operating
SNS	Oak Ridge, USA	1400	1.6×10^{16}	60	2006/Operating
JSNS	Tokaimura, Japan	1000	-	25	2008/Operating
ESS*	Lund, Sweden	5000	1.4×10^{17}	14	2019/Planned
IBR-2*	Dubna, Russia	-	2.26×10^{17}	5; 10	1984; upgrade 2011

*Long pulse neutron source

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