Neutron-diffraction studies at the JINR Laboratory of Neutron Physics

A. M. Balagurov
Joint Institute for Nuclear Research, Dubna

Fiz. Élem. Chastits At. Yadra **26**, 1619–1632 (November–December 1995)

The development of neutron-diffraction studies using pulsed sources at the Frank Laboratory of Neutron Physics of the JINR in the period from 1963 to 1995 is reviewed. F. L. Shapiro was directly involved in the initial stage of development of neutron-diffraction studies at the FLNP, and it was under his direction that the first experimental work was carried out. The special features of neutron-diffraction studies using pulsed neutron sources, the chronology of the main events in the development of this research at the FLNP, and the status of this research in the 1990s using the IBR-2 reactor are reviewed. © *1995 American Institute of Physics.*

Structural neutron-diffraction studies are usually concerned with using the technique of thermal-neutron diffraction to reconstruct the structure of an object (a crystal) with an accuracy sufficient for localizing individual atoms and for studying the structural rearrangements that occur under the influence of external conditions. In a broader sense, this area includes studies using the technique of small-angle neutron scattering, in which the resolution is at the level of individual atomic groups (~ 10 Å), and studies of an applied nature, for example, study of the texture and internal strains in bulk samples, and so on. The present review is devoted to the development of neutron-diffraction studies in the narrower sense using pulsed neutron sources at the Laboratory of Neutron Physics of the JINR, which began under the direction of F. L. Shapiro.

1. THE DA AND TOF DIFFRACTOMETERS

As is well known, neutron diffractometers at stationary reactors actually mimic the operation of the x-ray diffractometer: a monochromator sends a narrow ($\Delta\lambda/\lambda \approx 0.01$) line to a sample, and the diffraction spectrum is scanned in terms of the scattering angle. This is done by scanning an angular range either by a single detector or by a multi-counter or position-sensitive detector system. Neutron diffractometers of this type have come to be referred to as Double-Axis (DA) diffractometers, owing to the possibility of rotating the monochromator and the detector about two vertical axes.

Neutron-diffraction experiments can be performed quite differently from x-ray diffraction ones because the energy spectrum of thermal neutrons from a reactor is continuous (Maxwellian), the velocities of thermal neutrons are small, and it is possible to analyze the neutron energy (or wavelength) in terms of its time of flight.

These features were realized in the mid-1950s, which led to the design of Time-Of-Flight (TOF) neutron diffractometers.

The use of the time-of-flight method for studying neutron diffraction was apparently first suggested by Egelstaff in 1954.[1] The theoretical justification for neutron-diffraction studies using a broad spectrum of neutrons was given by Lowde in 1956,[2] but it was not until 1963–64 that the first experiments were performed using this technique at a stationary reactor with a pulse chopper in Świerk, Poland[3] and at the IBR-1 pulsed reactor at Dubna.[4] Until 1970 the theoretical and practical development of the method took place mainly at Dubna by a group of Russian and Polish physicists (V. V. Nitts, T. A. Machekhina, I. Sosnowska, J. Sosnowski, J. Leciejewicz, A. Holas *et al.*) under the direction of F. L. Shapiro and B. Buras.

2. SPECIAL FEATURES OF NEUTRON-DIFFRACTION STUDIES USING THE TIME-OF-FLIGHT TECHNIQUE

The functional scheme of the TOF diffractometer is standard for neutron spectrometers operating according to the time-of-flight technique: after being decelerated to thermal energies, neutrons from a pulsed source travel along a primary path, on which they are collimated and monochromatized. Then they are allowed to scatter on a sample, after which they are recorded at some fixed direction by a detector. An analyzer records the spectrum in a memory device with scanning in terms of the neutron time of flight from the moderator to the detector. The spectra from successive pulses of the source are added in order to accumulate sufficient statistics.

The most important consequence of using a continuous spectrum and the time-of-flight technique for scanning the diffraction pattern is a several-fold increase in the factor corresponding to the fraction of neutrons from the source which are used. As a result, in spite of the fact that the time-averaged neutron flux at existing pulsed sources is considerably smaller than at stationary sources ($\Phi = 1\times 10^{13}$ n/cm^2/sec for the IBR-2 at JINR and $\Phi = 1.5\times 10^{15}$ n/cm^2/sec for the HFR, ILL, Grenoble), the rate of accumulating diffraction data is comparable, and for some special types of experiment it can be many times higher when a TOF diffractometer is used.

The range of wavelengths used at a TOF diffractometer can be very broad. Usually it is 0.9–8 Å, but often very small wavelengths down to 0.5 Å and very large ones up to 20 Å are used. This makes it possible to cover a wide range of interplanar spacings using a small number of detectors. In fact, according to the Bragg law $d = \lambda/(2\sin\theta)$, only two detectors located at scattering angles of 20° and 160° for wavelengths in the range $0.9 \leq \lambda \leq 8$ Å allow d_{hkl} to be observed in the range from 0.46 to 23 Å.

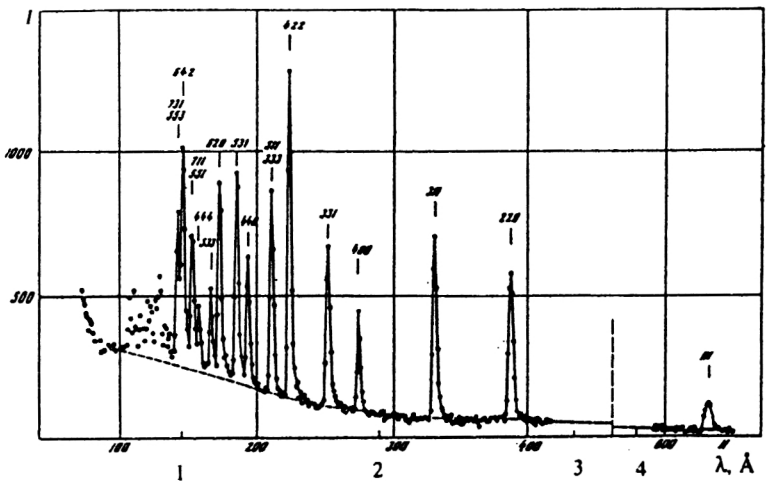

FIG. 1.

Using a TOF diffractometer it is easy to perform parallel one-, two-, or three-dimensional diffraction studies of the reciprocal space of a crystal. The time of flight gives the sweep along the radius vector of the reciprocal lattice, and the position groups of a one- or two-coordinate position-sensitive detector give the sweep in the transverse directions.

The resolution of a TOF diffractometer for polycystals can easily be reduced to $\Delta d/d = 0.003$, and in special cases even to 0.0005. It depends weakly on d_{hkl}, as a rule, improving with increasing d_{hkl}.

A traditionally noted feature of the TOF diffractometer is the possibility of making measurements in a fixed geometry, which is important, for example, when working with high-pressure chambers.

A serious drawback of the TOF diffractometer is that the data obtained is less precise than in the usual case. This is related to the need to introduce a large number of wavelength-dependent corrections in transforming the measured intensities of the diffraction peaks into structure factors. The most important of these corrections is the effective spectrum of neutrons incident on the sample, including the primary flight path and the detector efficiency. This correction can vary by a factor of ten, depending on the wavelength. The methods of determining it must still be considered faulty, and it is what essentially determines the accuracy of the experimental values of the structure factors of the crystal.

The first studies carried out at the Laboratory of Neutron Physics already confirmed many of the predicted advantages of the TOF diffractometer, in particular, the high rate of data collection. The pulsed nature of the irradiation of the sample by the neutron beam was specially noted in the studies by Shapiro *et al.*[5,6] This makes it possible to impose an external field on the sample in the pulsed mode, so that it is possible to greatly increase the amplitude of this field and reach values which are unattainable in the stationary mode. Depending on the duration of the (magnetic or electric) field pulse and the synchronization conditions, it is possible to observe its effect on the entire spectrum, on several diffraction peaks, or on a single peak. The study of relaxation processes using pulsed neutron sources appears to be very promising. In particular, it has been noted in Ref. 6 that when a high-intensity pulsed neutron source is used, it may be possible to obtain a complete neutron-diffraction pattern in a few minutes.

The further development of neutron diffraction studies at the Laboratory of Neutron Physics confirmed these predictions, and in some respects the predictions were even surpassed.

3. CHRONOLOGY OF THE MAIN EVENTS IN THE DEVELOPMENT OF NEUTRON-DIFFRACTION STUDIES AT THE LABORATORY

In **1963-64** the first methodological experiments were performed at the IBR-1. In these the time-of-flight method was used to measure the diffraction spectra from polycrystalline samples (Fig. 1).

In **1965** the first physics experiment was performed:[7] neutron diffraction was used to determine the orientation of the magnetic moments of the iron ions relative to the crystallographic axes in the compound $BiFeO_3$. The experiment was successful only because of a special feature of the TOF diffractometer: the improvement of the resolution with increasing d_{hkl}.

In **1966-67** an important methodological step was taken. Nearly simultaneously, Holas in Dubna and Carpenter at Argonne[8,9] suggested a method of time focusing allowing a significant increase in the luminosity of TOF diffractometers without worsening the resolution. This method was verified in practice in Dubna.[10]

In **1968** diffraction experiments were begun in which the sample was exposed to a strong pulsed magnetic field.[11]

Diffraction experiments were proposed in 1967 (Ref. 12) and then performed in **1968–70** (Refs. 13 and 14), in which the goal was to determine the amplitude for a neutron to interact with an electron associated with the nonzero rms charge radius of the neutron. These experiments are an example of the use of slow-neutron diffraction to measure constants of nuclear physics (coherent scattering lengths of neutrons on elements and isotopes) and constants directly related to the quark structure of nucleons.

In the late 1960s at the Laboratory, in connection with

the start of planning of the new, powerful IBR-2 pulsed reactor, I. M. Frank and F. L. Shapiro initiated a program of research on condensed-matter physics, with neutron diffraction playing an important role. It was proposed that the efforts be focused primarily on the solution of one of the most complicated problems of structural analysis: the determination of the structure of biological macromolecules. A structural neutron-diffraction group was organized in the division of condensed-matter physics (under the direction of Yu. M. Ostanevich) created in **1972** in order to study this problem and to develop techniques for structural analysis using the TOF diffractometer.

In **1974** this group completed the first trial quantitative experiment on a single crystal of $C_{10}D_8$ (Ref. 15), and in 1975 it performed an experiment to determine the positions of the deuterium atoms in the structure of the single crystal $La_2Mg_3(NO_3)_{12}24D_2O$ (Ref. 16).

In **1977** in collaboration with the Institute of Crystallography in Moscow (the Shuvalov Laboratory), diffraction studies were begun[17] to reveal the domain structure of ferroelectrics and ferroelastics. This research subsequently led to the development of multidimensional neutron-diffraction studies: first two-dimensional diffraction based on the use of a one-coordinate position-sensitive detector,[18] and then three-dimensional diffraction using a two-coordinate position-sensitive device.[19]

By **1982** most of the neutron spectrometers had been transferred from the IBR-30 to the IBR-2, and the first experiments using the multipurpose DN-2 diffractometer were begun. The diffractometer with pulsed magnetic field SNIM, the texture diffractometer NSVR, and the diffractometer for studying perfect crystals DIFRAN were introduced somewhat later. A neutron flux considerably larger than at the IBR-30, improved organization of the beams, and modern electronic controls led to qualitatively new possibilities in structural neutron-diffraction studies, so that many new subjects for research were found.

In **1983** the first experiments were performed with the DN-2 using biological objects: single crystals of globular myoglobin protein and multilamellar lipid membranes deposited on glass substrates. This initiated an extensive program of biological research. These experiments confirmed the possibility in principle of studying the structure of biological objects at the IBR-2. However, it was found that the sizes of single-crystal proteins accessible at that time were too small for full-fledged structural experiments, and, conversely, that multilamellar structures could be studied quite effectively.[20,21] The study of the structure of ribosomes and mycelar solutions using a small-angle scattering spectrometer became a second successful branch of this program of biological research.[22]

In **1985** systematic experiments were begun on the study of irreversible transient processes in condensed media using the technique of neutron diffraction in real time.[23,24] The high intensity of the neutron beam which could be obtained in the DN-2 diffractometer made it possible to successfully study transient processes with characteristic times of the order of several minutes.[25]

In **1989** it was decided that a high-resolution Fourier diffractometer[26] (HRFD) would be build at the IBR-2 for use in precision structural studies of polycrystalline materials. The work was carried out in collaboration with the PIYaF in Gatchina (the Trunov Laboratory) and the Technical Research Center of Finland (the Hiismaki Laboratory), and in 1992 the first high-resolution ($\Delta d/d \approx 0.0013$) diffraction spectra were recorded.[27]

In **1992** at the suggestion of V. A. Somenkov (of the RNTs, Kurchatov Institute), work began on the construction of the first in a series of specialized diffractometers for structural studies at high pressures (up to ~ 20 GPa).[28] The work on the DN-12 was completed at the end of 1993.

4. STRUCTURAL NEUTRON-DIFFRACTION STUDIES AT THE IBR-2 IN THE 1990S

The large number of neutron-diffraction studies of widely varying types being carried out at present at the IBR-2 can be divided into four groups of experiments, each requiring a particular diffractometer scheme. These are: experiments on single crystals, structural experiments on polycrystals, studies of transient processes in crystalline materials, and experiments using microscopic samples, usually at high pressure.

The modern TOF diffractometers used in studies of these types must have the following features (in the order of the four groups of experiments): the presence of a two-coordinate position-sensitive device with good (~ 0.3 cm) spatial resolution; high luminosity and high (at the level 0.001) resolution in $\Delta d/d$; very high luminosity and a very wide range in d_{hkl}; and very high luminosity with very large effect-to-background ratio.

The TOF diffractometers existing at the IBR-2: the DN-2, the HRFD, and the DN-12, allow structural experiments to be carried out at a level equal to and sometimes better than any in the world.

4.1. Studies of single crystals

It was noted above that the precision of the structural data obtained using TOF diffractometers is somewhat worse than than from DA diffractometers, owing to the need to introduce corrections strongly dependent on the neutron wavelength. Therefore, the main emphasis in studies of single crystals using TOF diffractometers is on experiments which realize the primary advantage of these diffractometers: the possibility of simultaneously scanning a large volume of the reciprocal space for a fixed geometry.

This has already been done for many years now with the DN-2 diffractometer using a linear position-sensitive device, and a large number of individual experiments and several large-scale research projects have been carried out using it. In the first of these, begun at the IBR-30, the domain structure of ferroelectric (KD_2PO_4 and $LiKSO_4$) and ferroelastic ($KD_3(SeO_3)_2$ and K_2ZnCl_4) crystals and their behavior under external perturbations were studied. In Fig. 2 we show an example of a measured intensity distribution at one of the sites of the reciprocal lattice of the KD_2PO_4 crystal in the ferroelectric (and simultaneously ferroelastic) phase.

Another case in which continuous scanning of the reciprocal space is necessary is that of studies of incommensurate

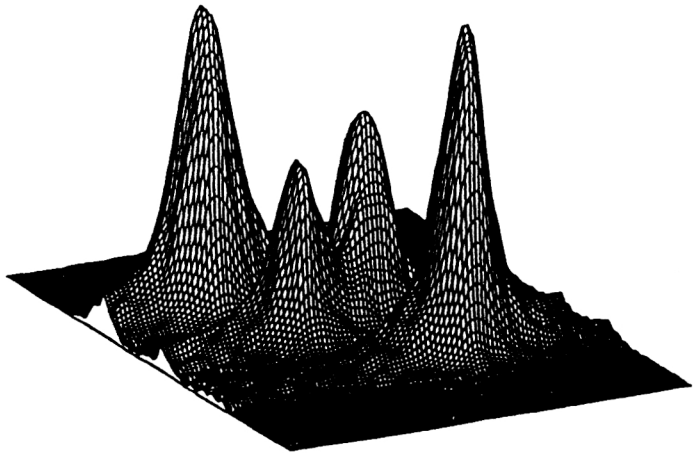

FIG. 2.

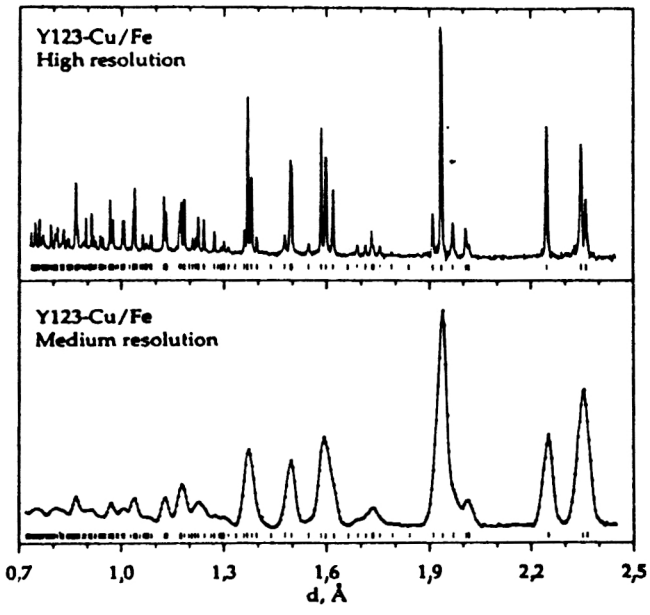

FIG. 3.

modulation of the structure (atomic or magnetic) and transitions between the commensurate and incommensurate phases of a crystal. Experiments have been carried out using the dielectric crystals $Sr_{1-x}Ba_xNb_2O_6$ (Ref. 30), the magnetic hexaferrites $Ba(Ti,Co)_2Fe_8O_{19}$ (Ref. 31), and high-temperature superconducting crystals of the type Bi-2212 (Ref. 32).

A somewhat unusual application of the continuous-scanning method is for the study of thermal diffuse scattering using a TOF diffractometer.[33]

4.2. High-resolution studies of polycrystals

The uniqueness of the IBR-2 reactor as a neutron source is manifested primarily in its thermal-neutron flux per pulse, which is the highest in the world. At the same time, it has been assumed that experiments requiring good resolution in the energy or the neutron wavelength are nearly impossible to carry out at the IBR-2, owing to the large width of the fast neutron pulse. It is possible to decrease the time component of the resolution function either by increasing the flight path or by somehow decreasing the pulse width. The designers of the NSVR spectrometer at the IBR-2 followed the first route: a flight path nearly 100 m long made it possible to obtain $\Delta d/d \approx 0.004$, which is sufficient for the texture experiments carried out using the NSVR. However, it was hoped that a level ~ 0.001 could be obtained, which would allow precision studies of the structure of polycrystals to be carried out. This proved possible with the help of the technique of correlation analysis using a fast Fourier chopper. In this method the effective width of the neutron pulse is inversely proportional to the maximum frequency of modulation of the neutron beam intensity and can be reduced to ~ 7 μsec. Here even for a path length of 20 m it is possible (in principle) to obtain $\Delta d/d \approx 0.0005$. Owing to the short flight path and high transmission of the Fourier chopper, the luminosity of this method significantly exceeds that of any other method in which such high resolution is obtained. The main drawback of the ordinary Fourier method, the high level of correlation background, is significantly suppressed, owing to the additional time strobing when this method is used with a pulsed neutron source.[27] The mock-up version of the HRFD diffractometer built in 1992 confirmed the correctness of all the ideas of the method; in particular, a level of resolution near 0.001 was obtained immediately. After the main components of the diffractometer were put in operation at the end of 1994, regular physics experiments were begun using it. The effect of the resolution obtained is shown in Fig. 3. Here we compare the diffraction spectra of $YBa_2Cu_{2.7}Fe_{0.3}O_7$ measured with the high-resolution Fourier diffractometer in the ordinary mode (lower figure) and by the Fourier method (upper figure).

We see that it was possible to radically improve the quality of the diffraction data and, accordingly, the structural information extracted. At the present time precision structural experiments[34] and studies of the internal strains in bulk samples and composite materials[35] are being carried out using the HRFD.

4.3. Diffraction experiments in real time

The special features of neutron diffraction make it an exceptionally powerful tool for studying transient processes in condensed media in real time, i.e., it is possible to follow structural changes occurring in the medium nearly without interruption. In the case of an irreversible process, for example, a chemical reaction, its observability is determined by the condition $t_s \ll \tau$, where τ is the characteristic time of the process and t_s is the time to measure a single diffraction spectrum with adequate statistics for the goals of the experiment. The value of t_s depends on the neutron flux in the primary beam, the area and scattering power of the sample, and the solid angle of the detector system, and for the neutron diffractometers with the highest luminosity at stationary reactors it is 5–15 min. Approximately the same times have been obtained at several pulsed neutron sources (ISIS, LANSCE). Using the DN-2 diffractometer at the IBR-2 reactor, it is possible to analyze irreversible processes in crystals with a time resolution of about 1 min, and individual

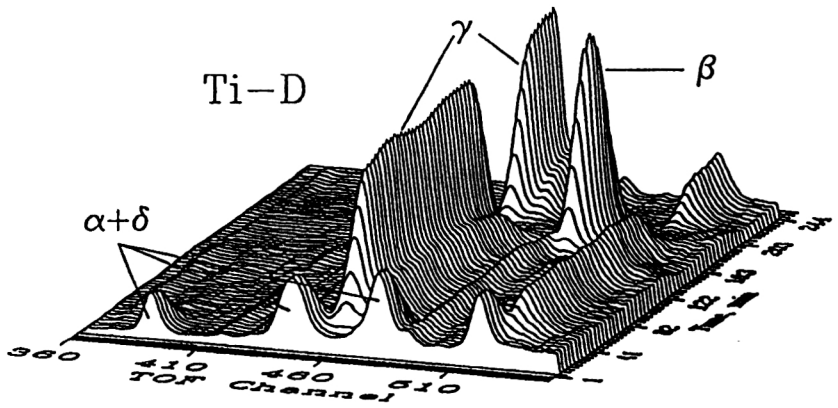

FIG. 4.

experiments have been performed with a resolution of 20 sec and even 2 sec (Ref. 36). An example of the evolution of the diffraction spectra during phase transitions in the $TiD_{0.73}$ system is shown in Fig. 4. Subsequent analysis of the set of spectra using the Rietveld method made it possible to determine the time (i.e., temperature) dependence of all the structural characteristics of the system.[37] In the last few years this method has been used at the DN-2 diffractometer to study a wide variety of processes: the hydration of cement,[23] synthesis of the compound Y123 (Ref. 38), amorphization of the compound Y123 when heated in a hydrogen medium,[39] phase transitions in heavy ice[40] and in the spinel $CuLi_{0.1}V_{0.1}Fe_{1.8}O_4$ (Ref. 41), and many others.

4.4. Studies of microscopic samples at high pressure

Until recently, the region of applicability of neutron-diffraction methods in studies of the behavior of matter at high pressures was, as a rule, limited to a range up to several GPa, owing to the use of relatively large (~ 1 cm^3) samples in pressure cells of the piston–cylinder type. It was completely impossible to obtain high pressures using an anvil, owing to the small (10^{-1}–10^{-3} mm^3) sample size and the relative weakness of the fluxes from neutron sources. However, during the last decade a method has been developed for carrying out neutron-diffraction studies at high pressure based on a combination of the techniques of diamond and sapphire anvils and high-luminosity, low-background neutron diffraction, so that the pressure range in these experiments could be extended up to several tens of GPa (Ref. 42). The experience gained in such experiments at the RNTs of the Kurchatov Institute was taken to the IBR-2, and in 1994 the DN-12 diffractometer was used to perform the first experiments. Careful extraction of the neutron beam and the original design of the detector system made it possible to come close to the world record in sample size and pressure, even using the relatively low-intensity reactor channel.[28] In Fig. 5 we show one of the measured diffraction spectra from a sample of $^{164}DyD_3$ in diamond anvils whose volume was only 0.027 mm^3. The DN-12 was used to carry out a series of interesting experiments in a short time, in particular, on the superconductor $HgBa_2CaCu_2O_{6+\delta}$ (Ref. 43), the molecular crystal NH_4Cl (Ref. 44), and so on.

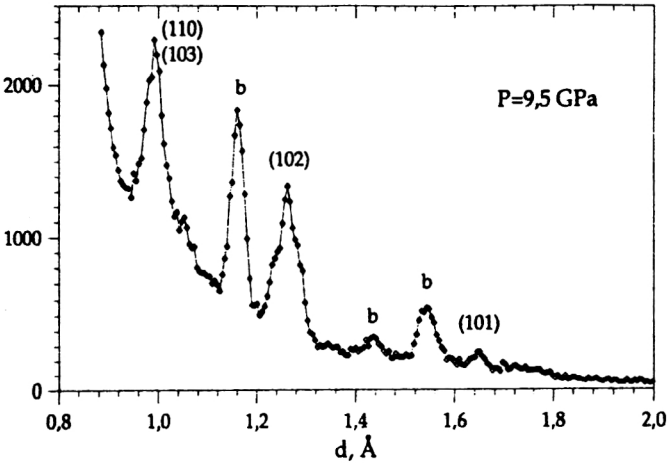

FIG. 5.

5. CONCLUSION

In recent years neutron-diffraction studies at the Laboratory of Neutron Physics have followed an amazing course of development, which was begun in the 1960s with the research of F. L. Shapiro and his students. The short-term perspectives are primarily related to improvement of already existing techniques. In 1995 at the DN-2 trials were begun of a two-coordinate position-sensitive device with resolution 0.3 cm, which will allow great progress in experiments on single crystals. The high-resolution Fourier diffractometer has been augmented by several additional detectors with large solid angle, which increases the diffractometer luminosity by several factors. A mirror neutron pipe will be installed at the DN-12 in 1996 for shaping the thermal neutron beam, and the single-ring detector will be replaced by an eight-ring one. This will permit a sharp decrease of the background and an increase of the luminosity.

It can be stated with certainty that, as it develops further, the diffractometer complex at the IBR-2 reactor will provide a powerful experimental base for solving practically any problems in modern structural neutron diffraction.

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Translated by Patricia A. Millard