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# Historical overview and introduction

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## 1. Prehistory

About one and a half decades after the discovery of the Mössbauer effect and after synchrotron radiation (SR) had been introduced as a new challenging tool discussions were started on the possibility of using SR as a source for Mössbauer experiments. One strong motivation was the high brilliance of SR, which was of particular importance for diffraction experiments [1]. Other distinct properties of SR, like pulse structure and tunability, promised new experimental possibilities like timed external perturbations and the use of parentless Mössbauer isotopes [2].

From these considerations, however, it was obvious that before SR could be used for nuclear resonance scattering experiments, the overwhelming background of nonresonant radiation had to be eliminated. A step towards the solution of this problem was to take advantage of the pulse structure of SR, allowing one to separate the delayed resonant scattering from the prompt nonresonant scattering [2,3]. Nevertheless, the overloading of the detectors by the prompt SR pulse was expected to be so tremendous that additional measures had to be taken to suppress the nonresonant radiation components. Different solutions were proposed [4–6], considering the particular properties which distinguish nuclear resonant scattering from nonresonant scattering, such as oscillator strength, polarisation dependence, and dependence on the directions of internal magnetic fields or electric field gradients.

Early experimental attempts to extract Mössbauer radiation from the $^{57}$Fe resonance from SR storage rings were doomed to failure. Little is known about them from publications except for attempts at pure nuclear Bragg scattering [5], a questionable claim for detection of delayed conversion electrons based only on gating off the electron detector and counting electronics [7], and theses describing tests of thin $^{57}$Fe single crystals and antireflection $^{57}$Fe mirrors [8] and tests of photomultiplier gating while scattering the beam over 90° [9]. The experimental situation at the end of the seventies is reflected by a first review on nuclear resonant experiments using SR [10]. These prehistoric studies are not covered in the present book.

In contrast to the slow progress of the experimental observations a lively and comprehensive theoretical development of the fundamentals of nuclear resonant dynamical diffraction by the groups of Yu. Kagan and A.M. Afanas'ev in Moscow and of G.T. Trammell and J.P. Hannon in Houston took place in the sixties and seventies. Their work was to serve later as a basis for experimental development, both for the observation of Mössbauer diffraction with conventional sources [11,12] and for the nuclear scattering of SR treated in this book. It should be stressed that besides the impact of the solid theoretical foundation, the personal interest and strong support by the theoreticians was decisive for the persistance of the experimentalists in these early years.

## 2. Since 1984: Nuclear Bragg Scattering (NBS)

As perceived at present, pure nuclear Bragg scattering turned out to be the most promising experimental approach. It yields the highest suppression of nonresonant radiation. The first experiment of this kind was reported by a Russian group, that used the antiferromagnetic order in an almost perfect single crystal of $^{57}Fe_2O_3$ [13] for the suppression of prompt scattering. Unfortunately, the experiment at a wiggler station of VEPP-3 (Colliding Electron–Positron Beams) was closed before enough data were collected to prove the effect [14]. In parallel one of the approaches of the Hamburg group was the first to be successful. It was also based on pure NBS, this time due to combined hyperfine interactions in a perfect single crystal layer of yttrium iron garnet (YIG) [15]. The combination of two such reflections gave sufficient suppression of the prompt radiation to yield the first convincing proof of nuclear resonant filtering of Mössbauer radiation from SR [16]. This breakthrough opened a new era of Mössbauer experiments.

In the following years, the group succeeded in observing in a single reflection geometry a quantum beat modulation of the time evolution, caused by interresonance interference in the presence of hyperfine splitting. This observation allowed the study of the crucial question of how precise the hyperfine parameters in single crystals, e.g., of YIG and $^{57}FeBO_3$, can be determined by NBS experiments. The first computer programs for the calculation of NBS time spectra were developed at that time. In parallel, coherent effects were investigated, which arise in collective nuclear excitation in Bragg and Laue geometry. Later, the field of timed perturbations in the ns-range was opened by studying switching the magnetization applied to the scattering crystal. The method of pure NBS was also applied to the resonance of $^{169}$Tm. All these experiments were performed using monochromatization down to about 4 eV and at count rates of order $1\,s^{-1}$ at the bending-magnet station F4 at HASYLAB (Hamburger Synchrotronstrahlungslabor).

The successful Hamburg experiment stimulated worldwide interest in nuclear resonant filtering of SR. The first to follow was a group at the Brookhaven National Laboratory (BNL), performing experiments mainly at a wiggler station of the Cornell High Energy Synchrotron Source (CHESS). The group introduced in the beam line an additional high-resolution monochromator, which reduced the energy bandwidth of the transmitted beam to about 6 meV. This monochromatization was sufficient to allow, for instance, the observation of pure NBS time spectra from a $^{57}Fe_2O_3$

single crystal right from time zero. A group at the Stanford Synchrotron Radiation Laboratory (SSRL) performed the first experiments with an undulator station at the Positron Electron Project (PEP), reaching unprecedented count rates of about 500 $s^{-1}$ in pure NBS from thin YIG single crystals. In these and in later experiments performed at CHESS, the group mainly studied effects of collective scattering in NBS. Likewise at CHESS and at the National Synchrotron Light Source (NSLS at BNL), a group from the Oak Ridge National Laboratory (ORNL) tried to develop neV-spectroscopy using Mössbauer radiation filtered by pure NBS. Finally, in the early nineties, a Japanese group managed to obtain at an undulator station of the TRISTAN accumulator ring in pure NBS from a $^{57}Fe_2O_3$ single crystal a count rate of the order of 14000 $s^{-1}$. Thus, within a period of about six years, NBS count rates using the $^{57}$Fe resonance were increased by four orders of magnitude, a progress primarily achieved by the high brilliance of undulators.

The experimental development in NBS and the theoretical description of the effects have previously been presented in two reviews of 1992 [17,18]. The advances of NBS are also briefly covered in the present issue, with emphasis on examples which show the particular information available in NBS experiments. The theory is given in sections III-1.1 and III-1.2, and the experimental part is described in section IV-1.1. The fields of scattering by multilayers and of grazing incidence reflection are reviewed in sections III-1.4 (theory) and IV-1.2–IV-1.3 (experiment).

## 3. Since 1990: Nuclear Forward Scattering (NFS)

Mössbauer radiation filtered by pure nuclear Bragg reflections could, in principle, be used as a recoilless multi-line source. For traditional Mössbauer spectroscopy on the energy scale this possibility had been analyzed in an early theoretical paper [19]. This approach was used, in fact, by the ORNL group in a search for quasi-elastic scattering [20], and a variant led to a single-line Mössbauer synchrotron source [21] (see section VII-3). Alternatively it had been proposed to extract the information about hyperfine interaction directly from the quantum beat (QB) modulation [22] in the time evolution of nuclear scattering. This idea turned out to be very attractive. In fact, the analysis of the hyperfine interactions via QB modulation had been successfully tested in the NBS experiments mentioned above. These measurements, however, at that time required single crystals of high quality, enriched in $^{57}$Fe, exhibiting pure nuclear Bragg reflections. It was of the highest importance to remove these severe restrictions on the sample material.

The problem was solved by using nuclear forward scattering (NFS). This method allows in a general way the study of the time evolution of nuclear scattering also from polycrystalline and amorphous materials. However, it was clear that standard monochromatization techniques applied so far would not be sufficient to suppress the giant nonresonant radiation in the forward direction, which exceeds the resonant part by roughly a factor $10^8$ in the case of $^{57}$Fe. Therefore, additional monochromatization was required.

For that purpose the Hamburg group investigated the possibility of additional broad-band nuclear resonant filters based on total reflection where suppression of the electronic channel was obtained by an antireflection coating (see, e.g., [23,24] and references therein). Even though these techniques have hardly been used for additional monochromatization so far, a field of research of its own was founded at that time. As for the monochromator, it turned out that the factor of about $10^3$ gained by the nonresonant high-resolution monochromator introduced by the Brookhaven group was sufficient. The performance of this monochromator had been demonstrated in an experiment, where the delayed nuclear scattering was measured in the presence of nonresonant charge scattering in an X-ray allowed Bragg reflection [25]. But the Brookhaven know-how about monochromators and the Hamburg ideas about NFS had to meet at a Gordon conference in 1989 before NFS could be successfully demonstrated in an experiment using $^{57}$Fe foils as targets at a bending-magnet station at the NSLS [26]. This experiment paved the way to general time differential Mössbauer spectroscopy using SR.

In the following years, the experimental conditions and techniques for NFS were essentially improved. For the high-resolution monochromator, a more compact and stable construction was achieved with a so-called “nested” geometry, which allowed one to overcome the mismatch between the emittance of premonochromators and the acceptance of high-resolution monochromators. For the detector, avalanche photodiodes (APD) were introduced, a new generation of ultrafast detectors practically without afterglow. As for the source, the third generation SR storage rings were constructed, the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, the Advanced Photon Source (APS) at Argonne, USA and the 8 GeV Super Photon ring (SPring-8) in Harima, Japan, each equipped with beam lines devoted to nuclear resonant scattering experiments.

In parallel with this development, fundamental properties and applications of NFS were investigated. For intensity reasons, targets with rather large effective thicknesses have to be used in NFS, where multiple scattering gives rise to an additional modulation, which in case of a single resonance is called dynamical beat (DB). In the presence of several resonances, QB and DB melt into hybrid forms of beating. Also of fundamental interest was the question of radiation coupling between several targets placed downstream behind each other. This question was also studied by external perturbation of the coupling by ultrasound. As for the applications, the particular properties of SR, like extremely small beam cross-section and linear polarization, were used for high-pressure experiments or studies of magnetic phase transitions, respectively. Also internal perturbations like relaxation and diffusion were investigated via NFS in a wide range of materials such as crystalline, biological and glassy samples.

NFS was also employed to test and apply the concept of a crossed polarizer/analyzer in combination with the optical activity of a nuclear scatterer placed in between to filter a beam of nuclear resonant radiation out of SR (see sections IV-3.2 and VII-1).

The experimental progress of NFS in the last years is covered by several contributions in the present issue. General features and fundamental aspects of NFS are discussed in sections II-2, III-1.1–III-1.3 and IV-2.1–IV-2.2. The application of NFS to traditional topics of Mössbauer spectroscopy like high-pressure physics, biology, and studies of relaxation and diffusion is presented in sections IV-2.3–IV-2.6. New topics, which only became possible by the special features of SR, like timed external perturbations or gamma-optics involving NFS, are described in sections IV-2.8 and IV-3.1–IV-3.4. The development of beam line optics, detectors and methodological developments are described in chapters VI and VII.

## 4. Since 1994: Nuclear Inelastic Scattering (NIS)

The tremendous increase of brilliance at the SR beamlines, achieved first in Japan at the TRISTAN accumulator ring in the early nineties [27], facilitated another unforeseen evolution: the measurement of phonon energy distributions. At resonance, nuclear inelastic scattering (NIS) had previously already been observed in the first experiments on incoherent nuclear scattering of SR [28]. The high brilliance of the beam line now facilitated the determination also of the energy dependence of this scattering channel and thus of phonon contributions [29]. From the NIS spectra, the phonon densities of states could be directly derived [30]. Thus the picture of a spike of recoilless radiation on top of a background distribution of recoil quanta, familiar to every Mössbauer spectroscopist from introductory textbooks, at last became reality.

After the pioneering experiment of a Japanese group the new method was implemented and improved at APS and ESRF. Precision and high resolution of the energy scan became the demanding criteria of this method. New monochromator designs made it possible to improve the energy resolution from 6 meV to less than 1 meV. This improvement was crucial for the resolution of different phonon modes, and in particular for the separation of low-energy modes from the elastic peak. The method has been applied so far to study lattice excitations in different solid state surroundings such as biological samples, nanocrystals and anisotropic crystals. The original method, which is sensitive to the partial densities of phonon states coupling to $^{57}$Fe-atoms, was later extended to determine also the total phonon density as observed by X-ray inelastic scattering.

Application of NIS to several parts of physics is presented in this book in section V-1. The topic of quasielastic scattering is dealt with in section V-2.1. Progress in monochromator design is described in sections VI-1 (small-band nonresonant filtering) and VII-2 (broad-band nuclear resonant filtering).

## 5. This issue

This issue is intended to give both an introduction to nuclear resonant scattering of SR and an overview over the progress achieved in this field in the last decade. It is a collection of articles written by authors almost all of whom are actively engaged in present-day research in this field. In the above historical overview three fundamental branches, NBS, NFS and NIS, were introduced to put some order in the methodological development. In the book itself a slightly different order is used.

The presentation starts with an introductory chapter (II), intended to give easy access to people not familiar with SR or with nuclear resonance scattering. Many of the statements or pictures in the articles of this chapter use a pedestrian approach. Any loose statements are followed, however, by a more precise formulation in the theoretical chapter.

In this chapter (III), first, the theoretical basis of coherent nuclear resonance scattering is formulated in sections 1.1–1.3, with special emphasis on NBS and NFS. The particular theoretical treatment of grazing incidence reflection and of scattering by multilayers is given in section 1.4. Internal perturbation of coherent scattering due to diffusion is addressed in section 1.5. Theoretical aspects of inelastic and incoherent scattering are given in sections 2.1–2.2.

Chapter IV covers the experimental investigation of coherent elastic nuclear scattering. Here, first experiments of NBS and the related scattering by multilayers or from thin films are presented in sections 1.1–1.3. Experiments aiming at basic features of NFS are discussed in sections 2.1–2.2. The use of NFS for the study of several classical fields of Mössbauer spectroscopy like high-pressure, biophysics, relaxation and diffusion is described in sections 2.3–2.6. The development of nuclear scattering of SR using non-iron isotopes is reviewed in section 2.7. Investigations of timed external perturbations of NFS by ultrasound are presented in section 2.8. Topics from resonant and nonresonant $\gamma$-optics like transverse coherence and polarization phenomena can be found in sections 3.1–3.2. Finally, studies of interferometry and backscattering are discussed in sections 3.3–3.4.

Chapter V covers the experimental investigation of inelastic and quasielastic nuclear scattering. After two general articles on NIS in sections 1.1–1.2, the present state of research in several fields is reviewed in sections 1.3–1.5. The related topic of quasielastic nonresonant scattering is described in section 2.

The next two chapters (VI and VII) are devoted to progress in beamline optics and to methodological developments. It is obvious how crucial technical progress is for the development and expansion of the field. Monochromator and detector techniques are described in sections VI-1–VI-2. In the following, alternative methods are sketched which are presently being developed. Pure NFS based on crossed polarizer/analyzer techniques is discussed in section VII-1. Highest-resolution monochromator techniques based on broad-band nuclear resonant scattering are reviewed in section VII-2. Production and properties of a single-line Mössbauer source achieved by pure NBS of SR at the Néel temperature are described in section VII-3. How to perform Mössbauer experiments using SR in a heterodyne technique can be found in section VII-4. Finally, in section VII-5 prospects of using nuclear resonant quanta for holography are described.

The last chapter (VIII) is devoted to data evaluation. In parallel with the increasing brilliance of the experimental stations and the ever increasing amount of data, it became important to reduce time-consuming computer programs to the extent that the data can be fitted as a matter of routine. The different available approaches to this problem are described in sections 1–5.

Even though the present collection of articles on nuclear resonant scattering of SR is quite comprehensive, there are still topics that have not been covered. This is, for instance, the case when first demonstration experiments have been performed. Here we mention nuclear small angle scattering, where the size of magnetic and electric domains and of domain walls may be studied [31]. Other topics are related to angular correlation, where one excites a nuclear level incoherently and follows the successive angular distribution [32] or de-excitation of the nuclear level through a cascade of nuclear levels, as in the case of $^{161}$Dy [33]. Also not touched are studies of external perturbations of nuclear excitons by acoustic vibrations in NBS [34,35] and by fast switching of the magnetization in NBS [36–38] and NFS [39,40]. Such experiments are of particular interest because of the possibility to produce superpositions of phased nuclear states which have an unusually long decay time [39].

The present overview of nuclear resonant scattering of SR can only give a snapshot on the state of the art in 1999. Looking back at what has been achieved every year in the past, we may attempt an extrapolation into the future and conclude that new and unexpected phenomena may well be found in the fruitful field of nuclear resonant scattering of synchrotron radiation in the course of its further expansion and development.

## References

[1] R.L. Mössbauer, Naturwissenschaften 60 (1973) 493.

[2] S.L. Ruby, J. Phys. 35 (1974) C6-209.

[3] E.J. Seppi and F. Böhm, Phys. Rev. 128 (1962) 2334.

[4] G.T. Trammell, J.P. Hannon, S.L. Ruby, P. Flinn, R.L. Mössbauer and F. Parak, in: *Workshop on New Directions in Mössbauer Spectroscopy*, ed. G. Perlow, AIP Conf. Proc., Vol. 38 (AIP, New York, 1977) p. 46.

[5] A.N. Artem’ev, V.A. Kabannik, Yu.N. Kazakov, G.N. Kulipanov, E.A. Meleshko, V.V. Sklyarevskii, A.N. Skrinsky, E.P. Stepanov, V.B. Khlestov and A.I. Chechin, Nucl. Instrum. Methods 152 (1978) 235.

[6] J.P. Hannon, G.T. Trammell, M. Mueller, E. Gerdau, H. Winkler and R. Rüffer, Phys. Rev. Lett. 43 (1979) 636.

[7] R.L. Cohen, G.L. Miller and K.W. West, Phys. Rev. Lett. 41 (1978) 381.

[8] M. Mueller, thesis, University of Hamburg (1980).

[9] C. Hermes, thesis, University of Munich (1981).

[10] R.L. Cohen, in: *Synchrotron Radiation Research*, eds. H. Winick and S. Doniach (Plenum Press, New York, 1980) p. 647; reprint in: *Mössbauer Spectroscopy II*, ed. U. Gonser (Springer, Berlin, 1981) p. 81.

[11] G.V. Smirnov, Hyp. Interact. 27 (1986) 203.

[12] G.V. Smirnov and A.I. Chumakov, in: *Resonant Anomalous X-ray Scattering, Theory and Applications*, eds. G. Materlik, C.J. Sparks and K. Fischer (Elsevier Science, Amsterdam, 1994) p. 609.

[13] G.V. Smirnov, V.V. Sklyarevskii, R.A. Voskanyan and A.N. Artem’ev, JETP Lett. 9 (1969) 70.

[14] A.I. Chechin, N.V. Andronova, M.V. Zelepukhin, A.N. Artem’ev and E.P. Stepanov, JETP Lett. 37 (1983) 633.

[15] H. Winkler, R. Eisberg, E. Alp, R. Rüffer, E. Gerdau, S. Lauer, A.X. Trautwein, M. Grodzicki and A. Vera, Z. Phys. B 49 (1983) 331.

[16] E. Gerdau, R. Rüffer, H. Winkler, W. Tolksdorf, C.P. Klages and J.P. Hannon, Phys. Rev. Lett. 54 (1985) 835.

[17] E. Gerdau and U. van Bürck, in [12], p. 589.

[18] J.P. Hannon and G.T. Trammell, in [12], p. 565.

[19] Yu. Kagan, A.M. Afanas’ev and V.G. Kohn, J. Phys. C: Solid State Phys. 12 (1979) 615.

[20] J.Z. Tischler, B.C. Larson, L.A. Boatner, E.E. Alp and T. Mooney, J. Appl. Phys. 79 (1996) 3686.

[21] G.V. Smirnov, U. van Bürck, A.I. Chumakov, A.Q.R. Baron and R. Rüffer, Phys. Rev. B 55 (1997) 5811.

[22] G.T. Trammell and J.P. Hannon, Phys. Rev. B 18 (1978) 165; Phys. Rev. B 19 (1979) 3835.

[23] J.P. Hannon, G.T. Trammell, M. Mueller, E. Gerdau, R. Rüffer and H. Winkler, Phys. Rev. B 32 (1985) 6374.

[24] R. Röhlsberger, E. Gerdau, M. Harsdorff, O. Leupold, E. Lüken, J. Metge, R. Rüffer, H.D. Rüter, W. Sturhahn and E. Witthoff, Europhys. Lett. 18 (1992) 561.

[25] J.B. Hastings, D.P. Siddons, G. Faigel, L.E. Berman, P.E. Haustein and J.R. Grover, Phys. Rev. Lett. 63 (1989) 2252.

[26] J.B. Hastings, D.P. Siddons, U. van Bürck, R. Hollatz and U. Bergmann, Phys. Rev. Lett. 66 (1991) 770.

[27] S. Yamamoto, X. Zhang, H. Kitamura, T. Shioya, T. Mochizuki, H. Sugiyama, M. Ando, Y. Yoda, S. Kikuta and H. Takei, J. Appl. Phys. 74 (1993) 500.

[28] U. Bergmann, J.B. Hastings and D.P. Siddons, Phys. Rev. B 49 (1994) 1513.

[29] M. Seto, Y. Yoda, S. Kikuta, X.W. Zhang and M. Ando, Phys. Rev. Lett. 74 (1995) 3828.

[30] W. Sturhahn, T.S. Töllner, E.E. Alp, X. Zhang, M. Ando, Y. Yoda, S. Kikuta, M. Seto, C.W. Kimball and B. Dabrowski, Phys. Rev. Lett. 74 (1995) 3832.

[31] Yu.V. Shvyd’ko, A.I. Chumakov, A.Q.R. Baron, E. Gerdau, R. Rüffer, A. Bernhard and J. Metge, Phys. Rev. B 54 (1996) 14942.

[32] A.Q.R. Baron, A.I. Chumakov, R. Rüffer, H. Grünsteudel, H.F. Grünsteudel and O. Leupold, Europhys. Lett. 34 (1996) 331.

[33] Y. Yoda, K. Sumitani, X.W. Zhang, I. Koyama, M. Yabashi and S. Kikuta, SPring-8 user experiments report No. 1 (1997) (JASRI, 1998) p. 51.

[34] Yu.V. Shvyd’ko, A.I Chumakov, G.V. Smirnov, V.G. Kohn, T. Hertrich, U. van Bürck, E. Gerdau, H.D. Rüter, J. Metge and O. Leupold, Europhys. Lett. 22 (1993) 305.

[35] V.G. Kohn and Yu.V. Shvyd’ko, J. Phys.: Condens. Matter 7 (1995) 7589.

[36] Yu.V. Shvyd’ko, A.I. Chumakov, G.V. Smirnov, T. Hertrich, U. van Bürck, H.D. Rüter, O. Leupold, J. Metge and E. Gerdau, Europhys. Lett. 26 (1994) 215.

[37] Yu.V. Shvyd’ko, T. Hertrich, J. Metge, O. Leupold, E. Gerdau and H.D. Rüter, Phys. Rev. B 52 (1995) R711.

[38] Yu.V. Shvyd’ko, E. Gerdau, U. van Bürck, P. Schindelmann, W. Potzel, T. Hertrich, V.G. Kohn and A.I. Chumakov, ESRF user’s report HE-183 (1997).

[39] Yu.V. Shvyd’ko, T. Hertrich, U. van Bürck, E. Gerdau, O. Leupold, J. Metge, H.D. Rüter, S. Schwendy, G.V. Smirnov, W. Potzel and P. Schindelmann, Phys. Rev. Lett. 77 (1996) 3232.

[40] S. Kikuta, Y. Yoda, I. Koyama, T. Shimizu, H. Igarashi, K. Izumi, Y. Kunimune, M. Seto, T. Mitsui, T. Harami, X. Zhang and M. Ando, in: *X-ray and Inner-Shell Processes*, eds. R.L. Johnson, H. Schmidt-Böcking and B.F. Sonntag, AIP Conf. Proc., Vol. 389 (AIP, New York, 1997) p. 351.