5. International Workshop on Nuclear Resonance Scattering of Synchrotron Radiation: Status, Highlights, Methodology, and Trends
A workshop jointly organised with the Sapphire Ultra Optics for Synchrotron Radiation Helmholtz-Russia Joint Research Group 402 driven by the FZ Jülich / DESY/ ESRF / KIT / Shubnikov IC RAS

21-23 September 2015; DESY Hamburg

BOOK OF ABSTRACTS

Pressure studies of Fe-based superconductors using ^{57}Fe Synchrotron Mössbauer Source

V. Ksenofontov[1], S.I. Shylin[1], S.A. Medvedev[2], S.J. Sedlmaier[3], S.J. Clarke[3], and G. Wortmann[4]

[1]*Institute of Inorganic and Analytical Chemistry, Johannes Gutenberg University Mainz, 55099 Mainz, Germany*
[2]*Max Planck Institute for Chemical Physics of Solids, 01187 Dresden, Germany*
[3]*Department of Chemistry, University of Oxford, Oxford OX1 3QR, United Kingdom*
[4]*Department of Physics, University of Paderborn, 33095 Paderborn, Germany*

Many experimental facts provide evidence that antiferromagnetic (afm) spin fluctuations can mediate superconductivity (SC) acting as “glue” for Cooper pairs in Fe-based superconductors [1,2]. Our recent Mössbauer studies of FeSe intercalated with Li/NH_3 spacer layers with a SC transition temperature of T_C = 42 K support this idea [3]. Additional studies at low temperatures demonstrate that beside the dominant doublet there is a pronounced magnetic subspectrum of dynamic nature. In this regard, this novel Li/NH_3-FeSe system with its high T_C could be considered as a clue compound for the understanding of the principal mechanisms of SC in Fe-based superconductors. These studies revealed that the intensity of this magnetic fraction increases when passing to the superconducting state. We also observed in resistivity studies a marked decrease of T_C with increasing pressure. Therefore we performed a detailed high-pressure Mössbauer study of Li/NH_3-FeSe using the ^{57}Fe Synchrotron Mössbauer Source (SMS) at beamline ID18 of ESRF. Here we used the advantage of high beam intensity, small (ca. 20 μm) beam cross section, most favorable for high-pressure experiments, and the absence of background in detection of the 14.4 keV γ-rays.. These features enabled us to use non-enriched high-quality samples prepared as described in [3]. These ^{57}Fe-SMS high-pressure studies revealed that the amount of magnetic fraction decreases and the frequency of the magnetic fluctuations increases with pressure (Fig. 1). These findings allow us to conclude that the pairing mechanism in FeSe-based superconductors is mediated by afm spin fluctuations. We performed also ^{57}Fe-SMS pressure studies of Cu-doped FeSe superconductor (20% ^{57}Fe-enriched $Fe_{0.97}Cu_{0.04}Se$). Doping of small amounts of Cu into the FeSe matrix suppresses SC and introduces local moments at the Fe sites, evidenced by glassy magnetic interactions [4]. Application of pressure leads to restoration of SC in Cu-doped FeSe [5]. High-pressure SMS studies of non-SC $Fe_{0.97}Cu_{0.04}Se$ revealed that this occurs because of the suppression of the spin-glass state.

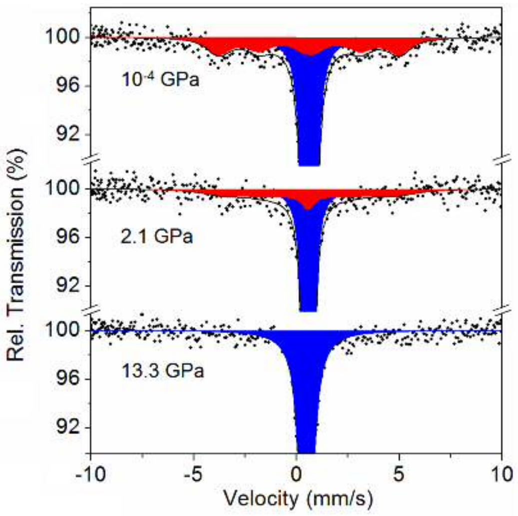


Figure 1: Mössbauer spectra of SC Li/NH_3 -FeSe measured with ^{57}Fe-SMS at different pressures (T = 3 K).

References

[1] D. J. Scalapino, Rev. Mod. Phys. **84**, 1383 (2012).
[2] Y. Imai, et al., Phys. Rev. Lett. **102**, 177005 (2009).
[3] S. I. Shylin, et al., Europhys. Lett. **109**, 67004 (2015).
[4] A. Williams, et al., J. Phys.: Condens. Matter **21**, 305701 (2009).
[5] L. M. Schoop, et al., Phys. Rev. B. **84**, 174505 (2011).

Nuclear Resonant GISAXS: Disentangling heterogeneous magnetic behavior in a nanopatterned Fe thin film

D. Erb[1], *K. Schlage*[1], *H.-C. Wille*[1], *R. Rüffer*[2], *and R. Röhlsberger*[1]

[1] DESY, Notkestr. 85, 22607 Hamburg, Germany
[2] ESRF, BP 220, F-38043, Grenoble CEDEX, France
(denise.erb@desy.de)

Nanopatterned magnetic materials are of considerable interest for both academic research and industrial application. We present a novel technique, combining Nuclear Resonant Scattering (NRS)[1] and Grazing Incidence Small Angle X-ray Scattering (GISAXS)[2], which allows disentangling the magnetic properties of distinct structural units in a nanopatterned system. The underlying idea is to exploit the fact that the nuclear resonant signal (carrying the magnetic information) undergoes the same scattering in q-space as the electronic signal (carrying the structural information). Thus, photons scattered non-resonantly or resonantly from different structural units of the sample are separated due to the sample morphology and can be detected at different positions in the scattering pattern. To demonstrate this principle, we fabricated a sample, in which structural and magnetic heterogeneity are correlated: A substrate with parallel surface facets was prepared by high-temperature annealing of M-plane sapphire. Sputter deposition of ^{57}Fe onto this substrate under non-normal incidence resulted in a continuous hardmagnetic ^{57}Fe film in which stripe-like regions of different thicknesses alternate. We investigated this sample in-situ during ^{57}Fe film growth (beamline ID18, ESRF) and studied its response to external magnetic fields ex-situ (beamline P01, PETRA III). During film growth we observed the onset of ferromagnetic ordering first in the thicker regions, then in the thinner regions. Upon applying an external magnetic field the magnetic moments in thick and thin regions are displaced from the easy axis of magnetization to different extents [3]. Thus we have demonstrated that nuclear resonant GISAXS can be a feasible method for obtaining information about the magnetic state of individual parts of a magnetically heterogeneous sample.

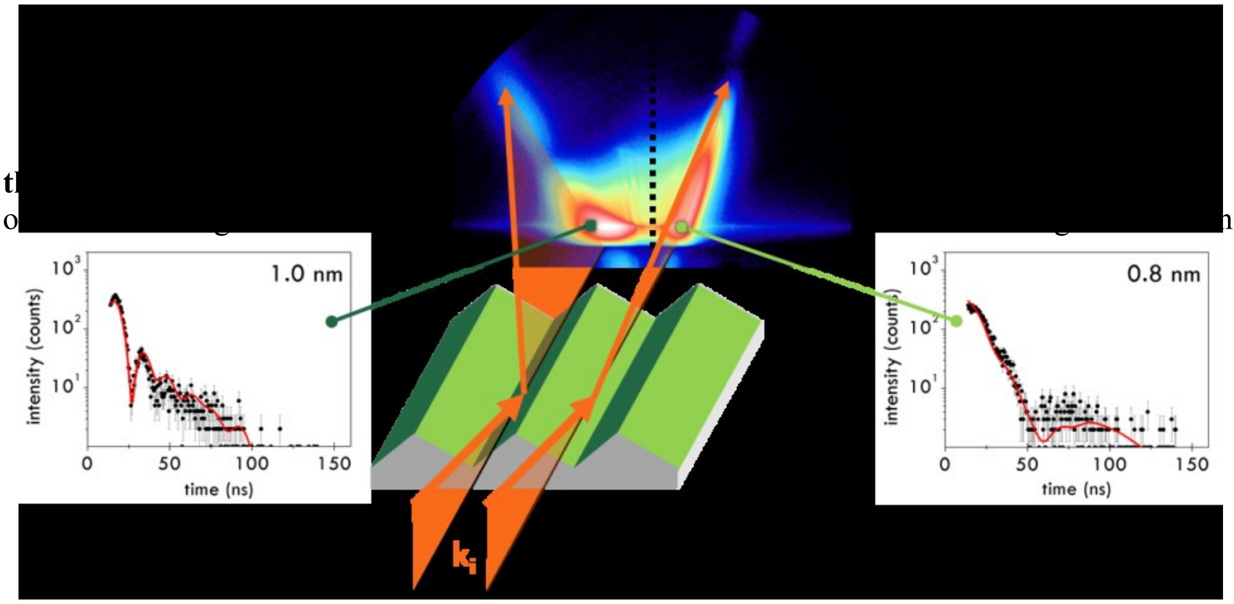


Figure 1: Illustration of the NR-GISAXS principle with exemplary GISAXS pattern and NRS time spectra. The sample is a ^{57}Fe thin film with periodically varying thickness on a faceted α-Al_2O_3 substrate.

References

[1] R. Röhlsberger, Springer Tracts in Modern Physics 208 (2004)
[2] G. Renaud, R. Lazzari, and F. Leroy, Surface Science Reports 64 (2009) 255
[3] D. Erb, Ph.D. thesis, University of Hamburg (2014)

Exploring new isotopes using Nuclear Resonance Scattering

D. Bessas

European Synchrotron Radiation Facility, F-38043 Grenoble, France

Nuclear resonance scattering of synchrotron radiation – comprising of nuclear forward [1,2] and nuclear inelastic scattering [3,4] – is a well established technique for obtaining information related to the hyperfine interactions and the lattice dynamics, respectively. It is a particularly useful technique when Mössbauer spectroscopy is impractical, *e.g.*, when a relevant radioactive source does not exist or its lifetime is short, when the experimental setup requires a collimated or small-size beam, or when element specific lattice dynamical characterization is required.

In this talk nuclear resonance scattering of synchrotron radiation by the newly introduced ^{187}Os [5] and ^{99}Ru [6] first nuclear excited states will be presented and further hints on exploring new isotopes, such as Hf, Gd, *etc,* will be given.

The low transition energy, 9.778(3) keV, of ^{187}Os in combination with its high nuclear mass leads to a high recoil free fraction, f_{LM}=0.95(1) at room temperature. Such high f_{LM} allows for extracting the density of phonon states from nuclear inelastic scattering measurements at room temperature even on Os organometallics.

Characteristic nuclear forward scattering spectra from the highest *ever* transition energy measured, *i.e.*, 89.671(3) keV, will be shown and relation with potential applications will be given. This paves the way for nuclear resonance scattering of synchrotron radiation by several other high-energy Mössbauer transitions with E~90 keV.

References

[1] J. B. Hastings, *et al.*, Phys. Rev. Lett. **66**, 770 (1991).
[2] U. van Burck, *et al.*, Phys. Rev. B **46**, 6207 (1992).
[3] M. Seto, *et al.*, Phys. Rev. Lett. **74**, 3828 (1995).
[4] W. Sturhahn, *et al.*, Phys. Rev. Lett. **74**, 3832 (1995).
[5] D. Bessas, *et al.*, Phys. Rev. B **91**, 224102 (2015).
[6] D. Bessas, *et al.*, Phys. Rev. Lett. **113**, 147601 (2014).

Synchrotron Based NRS Techniques and Evaluation

W. Sturhahn

Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA

The discovery of nuclear resonant scattering (NRS) using a synchrotron radiation source by *Gerdau et al.* in 1985 [1] was followed by intense development that was fuelled by availability of third-generation synchrotron facilities: the ESRF in Grenoble, France; the APS in Argonne, USA; the SPring-8 in Hyogo, Japan, and more recently PETRA III in Hamburg. A variety of NRS were explored during the earlier period and some have survived the test of practicality and are in use today for applications such as the study of vibrational and magnetic properties of condensed matter under extreme conditions. In this presentation, a selection of NRS techniques is reviewed with emphasis on their potential for applicability and availability of evaluation software.

The scheme in Figure 1 illustrates how four classes of NRS are distinguished: coherent elastic (I); incoherent elastic (II); incoherent inelastic (III). Each class has seen development of specific tools as shown in Table I that have been used in a variety of applications, and superior brightness and focused spectral flux density of third-generation synchrotron radiation facilities has permitted scientists to develop applications with ever smaller samples under increasingly extreme conditions.

Early nuclear resonant scattering studies showed that synchrotron radiation experiments with nuclear resonances greatly benefitted from a new, translational approach: time resolved instead of energy resolved measurements, the latter familiar to traditional Mössbauer spectroscopy. This advance resulted from the time structure of synchrotron radiation, which is emitted as a sequence of very short x-ray pulses of typically less than 100 ps duration. Energy spectroscopy in the μeV to neV range is possible by analysis of the time-decay pattern of x-rays scattered off or transmitted through samples containing a suitable nuclear resonant isotope. The measurement and analysis of such time spectra constitutes the main part of the NFS/SMS, GINRS, NBS/NLS, NLE, and SRPAC methods. NRIXS on the other hand, integrates time spectra but nevertheless requires time discrimination.

Nuclear resonant scattering science continues to evolve with enhanced instrumentation, improvement of synchrotron radiation sources, development of nuclear resonant methods, and new applications. Almost always scientific results rely critically on tested and easily accessible evaluation software, such as the CONUSS and PHOENIX programs [3]. Continuous maintenance of software and proper hands-on training to potential users are very important to optimize user experience.

Table I: Nuclear resonant scattering tools and classes. Abbreviations: Nuclear Resonant Inelastic X-ray Scattering (NRIXS); Nuclear Resonant Vibrational Spectroscopy (NRVS); Nuclear Forward Scattering (NFS); Synchrotron Mössbauer Spectroscopy (SMS); Grazing Incidence Nuclear Resonant Scattering (GINRS); Nuclear Bragg/Laue Scattering (NBS/NLS); Nuclear Lighthouse Effect (NLE); Synchrotron Radiation Perturbed Angular Correlation (SRPAC); traditional Mössbauer Spectroscopy (MS).

tool	I	II	III
NRIXS/NRVS	-	-	X
NFS/SMS	X	-	-
GINRS	X	-	-
NBS/NLS	X	-	-
NLE	X	-	-
SRPAC	-	X	X
MS	-	X	X

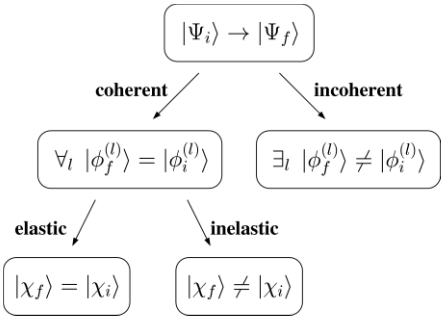


Figure 1. Classification of scattering processes.
The quantum state of the scatterer $|\Psi\rangle$ is factorized into quantum states of the atom cores $|\phi\rangle$ and vibrations $|\chi\rangle$.
(adapted from [2])

[1] E. Gerdau et al., Phys. Rev. Lett. 54, 835-838 (1985).
[2] W. Sturhahn, J. Phys.: Condens. Matter 16, S497-S530 (2004).
[3] http://www.nrixs.com

Possible problems in the determination of the mean sound velocity from the density of vibrational states

A.I. Chumakov

European Synchrotron Radiation Facility, F38043, Grenoble France

Measurement of the density of vibrational states (DOS) via Inelastic X-ray Scattering (IXS) and Nuclear Inelastic Scattering (NIS) offers a useful means for the determination of the mean sound velocity. If, in addition, the density and compressibility data are available, this also allows for the determination of both the transverse and longitudinal sound velocities, and of the corresponding shear and longitudinal elastic moduli.

A proper determination of the mean sound velocity from the IXS and INS data requires *(i)* a correct derivation of the DOS from the inelastic scattering spectra, *(ii)* a correct determination of the coefficient of the parabolic-like dependence of the DOS in the low-energy region (i.e., the so-called Debye level) from the derived DOS, and *(iii)* a correct calculations of the mean sound velocity from the determined Debye level. We analyze the possible problems which may arise in every step of the data processing. The analysis is performed with the examples of the NIS data, but it is directly relevant also for the IXS data.

The analysis is summarized by the estimations of the uncertainties in the calculated mean sound velocity related to various stages of the data treatment, by revealing the most typical sources of problems, and by emphasizing the most robust approaches in the data analysis.

Finally, we discuss some cases where the mean sound velocities estimated from the DOS do NOT agree with those obtained by other methods (e.g., from dispersion relations or from ultrasound measurements), and show that such a discrepancy may provide important information about the studied systems.

NRIXS data analysis

Michael Y. Hu

Argonne National Laboratory, Argonne, Illinois, USA

Nuclear Resonant Inelastic X-ray Scattering (NRIXS) is a spectroscopy method to study atomic vibrations and dynamics, currently done with synchrotron radiation at a few high energy third generation facilities. It finds a wide range of applications in condensed matter physics, materials science, chemistry, biophysics, geosciences, and high-pressure researches. Many atomic dynamics and lattice thermodynamics information can be derived from NRIXS measurements. Phonon Density of States (DOS) characterizes lattice dynamics of a material and can be derived under the quasi-harmonic approximation. Combined with modeling and simulations, results from NRIXS can provide unique and clarifying insights into many fields of research. As for a spectroscopic technique, in order to be able to provide reliable information, close attention should be paid to many issues during experiments and data analysis afterwards. Here we discuss spectrum and DOS normalization, background, elastic peak, energy scale, and error estimations Types of information that derived from NRIXS measurements are summarized. We consider the extraction of sound velocity and moments of the spectrum in applications. Common practices and software used in NRIXS data analysis are also discussed.

Development of ^{61}Ni SR Mössbauer spectroscopy for studying nickel containing enzymes

Lars Lauterbach[1,2], Leland B. Gee[1], Francis E. Jenney, Jr.[3], Ann Ploskonka[4], Yoshitaka Yoda[5], Ryo Masuda[6], Makina Saito[6], Yasuhiro Kobayashi[6], Marius Horch[1], Ingo Zebger[1], Christian Teutloff[8], Mike Adams[9], Hannah Shafaat[10], Kenji Tamasaka[11], Charles Riorden[4], Oliver Lenz[1], Makoto Seto[6,7], Stephen P. Cramer[1]

[1]Department of Chemistry, University of California, Davis, One Shields Ave, Davis, CA 95616, USA; [2]Institute for Chemistry, PC14, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany; [3]Georgia Campus – Philadelphia College of Osteopathic Medicine 625 Old Peachtree Road NW Suwanee, GA 30024, USA; [4]Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, USA; [5]JASRI, SPring-8, 1-1-1 Kouto, Mikazuki-cho, Sayo-gun,Hyogo 679-5198, Japan; [6]Research Reactor Institute, Kyoto University, Kumatori-cho, Sennan-gun, Osaka 590-0494, Japan; [7]Japan Atomic Energy Agency, Mikazuki-cho, Sayo-gun, Hyogo 679-5148, Japan [8]Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Berlin, Germany; [9]Department of Biochemistry & Molecular Biology Life Sciences Building, Green Street, University of Georgia, Athens, Georgia 30602-7229, USA Department of Chemistry and Biochemistry, [10]The Ohio State University, 100 West 18th Ave. Columbus, OH 43210-1340 USA [11]RIKEN, SPring-8, 1-1-1 Kouto, Mikazuki-cho, Sayo-gun, Hyogo 679-5198, Japan

Nickel is an important earth-abundant transition metal for chemical and enzymatic catalysis [1,2]. In nature, nickel containing hydrogenases catalyze the reversible interconversion of molecular hydrogen to protons and electrons, a reaction with significant relevance towards alternative energy storage and carbon-neutral fuels.

One critical challenge in characterizing the reaction mechanisms of [NiFe] hydrogenases lies in identification of the oxidation and spin state of the nickel center in each catalytic state, which are proposed to include both high - and low-spin - Ni(II), Ni(III) and most likely Ni(I) [3]. Simple active site models of hydrogenases can be obtained by metal cofactor replacement within natural electron transfer proteins. One such model is nickel-substituted rubredoxin (NiRd) from *Pyrococcus furiosus*, which has an oxidized state that resembles the EPR-active forms of [NiFe] hydrogenases and reduced state similar to the Ni(II) high spin EPR-silent state [3,4,5].

In order to obtain insights into the electronic structure of the nickel containing active site, we have performed synchrotron radiation (SR)-based Mössbauer spectroscopy (MB) at BL09XU and BL19LXU (SPring8) on nickel model compounds, NiRd, and the oxygen tolerant regulatory hydrogenase from *Ralstonia eutropha*. The deployed SR-MB setup was first developed by Seto's group for other transition metals, including ^{57}Fe and ^{73}Ge [6]. To make "dilute" biological samples feasible for ^{61}Ni-SR-MB, a cryostat allowing up to 20 cm path length was constructed, all samples were enriched with ^{61}Ni and the SR-MB detector system was improved.

Here we report, to the best of our knowledge, the first ^{61}Ni-SR-MB spectra of biological samples. The results will be discussed with respect to nickel hyperfine parameters [7] and the prospects of ^{61}Ni-SR-MB will be reviewed.

Reference:

[1] S.Z. Tasker, E.A. Standley, T.F. Jamison, Nature **509**, 299-309 (2014)

[2] S.W. Ragsdale, J. Biol. Chem. **284**, 18571-18575 (2009)

[3] W. Lubitz, H. Ogata, O. Rüdiger, E, Reijerse, Chem. Rev. **114**, 4081-4148 (2014)

[4] F. E., Jr. Jenney, M. W. Adams, Methods. Enzymol. **334,** 45-55 (2001)

[5] L. Lauterbach**,** H. Wang, M. Horch, L.B. Gee, Y. Yoda, Y. Tanaka, I. Zebger, O. Lenz, S.P. Cramer, Chem. Sci. **6**,1055–1060 (2015)

[6] M. Seto, R. Masuda, S. Higashitaniguchi, S. Kitao, Y. Kobayashi, C. Inaba, T. Mitsui, Y. Yoda, Phys. Rev. Lett. **102**, 217602-217604 (2009)

[7] I. Sergueev, A. I. Chumakov, T. H. Deschaux Beaume-Dang, R. Rüffer, C. Strohm, U. van Bürck, Phys. Rev.Lett. **99**, 0976011-0976012 (2007)

Analysis Procedure of a Series of Nuclear Forward Scattering Experiments

V. Vrba, V. Procházka, and M. Miglierini[1]

Faculty of Science, Palacky University, 771 46 Olomouc, Czech Republic

[1]*Institute of Nuclear and Physical Engineering, Slovak University of Technology, 812 19 Bratislava, Slovakia*

Nuclear forward scattering (NFS) of synchrotron radiation is a suitable technique for in-situ observation of phase transformations or chemical reactions. Using ^{57}Fe enriched samples the time of one interferogram accumulation decreases below one minute. This technique was sucessively applied to inspect details of crystallization in amorphous alloys [1] under dynamic and isothermal heating conditions as well as chemical decomposition of high valent iron compounds. The duration of both processes is from one to two hours. However, such in-situ NFS experiments usually provide about one hundred or even more interferograms that have to be properly evaluated. In Figure 1, an example of crystallization process followed by in-situ NFS in a $^{57}Fe_{81}Mo_8Cu_1B_{10}$ metallic glass is presented in a form of contour plot. The abscissa represents time delay after the excitation synchrotron pulse while the y-axis shows heating temperature.

The evaluation of a huge number of the interferograms (~ 130), which were acquired every 60 s, was performed by the CONUSS code [2]. In order to solve this challenging task a sort of an user-interface and control code called HUBERT was elaborated. It allows analysis of a sequence of NFS experiments. The evaluation is based on an assumption that the neighbouring spectra differ one from another only slightly and also that their hyperfine parameters are similar and evolve smoothly with time (and/or temperature). The idea is to use the best result of one fit as starting values for the hyperfine parameters of the following fit. The first spectrum is evaluated manually and when the fitting model is correct the evaluation of the rest interferograms proceeds automatically. Nevertheless, possible weak points of such approach should be considered. For example, the time/temperature dependencies of the fitted hyperfine parameters could exhibit some hysteresis when progressing along ascending or descending time/temperature, i.e. when starting the fits from one or from the other side of the sequence of interferograms. In addition, possible difficulties occur when the change in neighbouring sets of some parameters is too high and/or abrupt. Such situation is encountered in a vicinity of magnetic ordering transition (e. g., close to Curie temperature). In such case the automatic fitting procedure fails and manual intervention is needed. Details on the suggested fitting procedure including discussion related to the reliability of such evaluation process and the obtained results are presented.

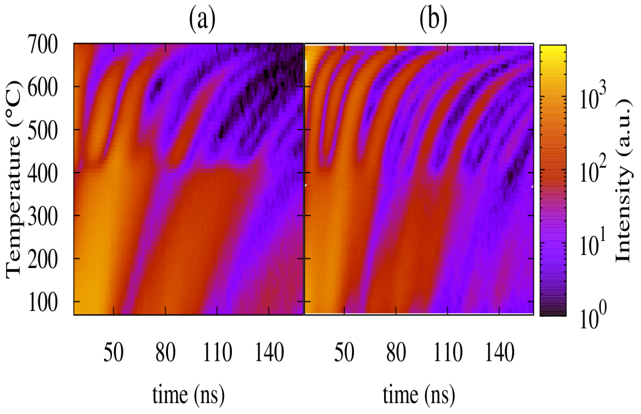


Figure 1: NFS in a $^{57}Fe_{81}Mo_8Cu_1B_{10}$ metallic glass without (a) and with external magnetic field (b).

References

[1] V. Procházka, V. Vrba, D. Smrčka, R. Rüffer, P. Matúš, M. Mašláň, and M. Miglierini, J. Alloy. Compounds **638**, 398 (2015).

[2] W. Sturhahn, E. Gerdau, Phys. Rev. B 49 (1994) 9285.

Control of polarization-encoded x-rays at single-photon nuclear interfaces

J. Gunst, C. H. Keitel, and A. Pálffy

Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, D-69117 Heidelberg, Germany

The interplay between optical lasers and atomic transitions has dominated the world of quantum physics over the last decades. New x-ray light sources like x-ray free-electron lasers (XFEL) together with the recent progress in x-ray optical elements open up this domain for higher photonic energies and strongly push forward the upcoming field of x-ray quantum optics [1]. In addition, the highly brilliant XFEL beams are expected to render the resonant driving of nuclei embedded in solid-state targets efficient via direct and secondary processes [2]. Thereby, the coherent control of the x-ray nucleus interaction is not only of fundamental interest but also builds the basis for many promising applications like for instance in information technology [3]. There, the extension to shorter wavelengths would drastically decrease the natural constraint on compact photonic devices set by the diffraction limit of the operating light [4]. However, in order to exploit orthogonal polarization states of x-rays as information encoding, control schemes performed on the single photon level are required, rarely available yet. Therefore, we investigate theoretically how to coherently manipulate the polarization properties of x-rays in the course of nuclear forward scattering (NFS) on ensembles of ^{57}Fe nuclei in an external magnetic field.

Since the 14.4 keV Mössbauer transition of the ^{57}Fe nuclei precedes recoillessly, resonant x-ray scattering occurs via a delocalized excitation in the nuclear target which leads to a high directionality of the scattering process into the forward direction. We use that the polarization response of this collective excitation can be dynamically manipulated by rotations of the external magnetic field [5] as illustrated in Figure 1. Fast rotations of the hyperfine fields induce an abrupt redistribution of the nuclear excitation among the Zeeman levels which can lead to constructive or destructive interferences between certain hyperfine transitions. It turns out that by applying these rotations temporally synchronized with the nuclear excitation event it is possible to switch between orthogonal polarization states of the scattered x-rays. For a fixed B-field geometry the polarization response is completely determined by the moment of rotation. In this way we are able to perform logical operations on polarization-encoded x-rays by using a single setup.

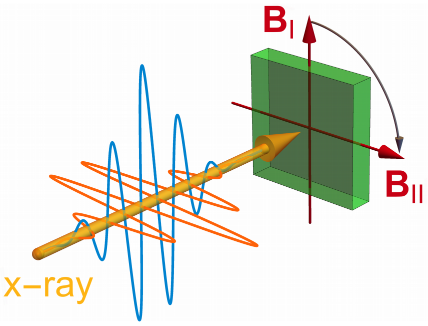


Figure 1: NFS setup. Either σ- (orange) or π-polarized (blue) x-rays are scattered on a nuclear sample and detected in forward direction. The polarization response is controlled by the B-field rotation from $\mathbf{B}_{\mathrm{I}}$ to $\mathbf{B}_{\mathrm{II}}$.

References

1 B. W. Adams *et al.*, J. Mod. Opt. **60**, 2 (2013).
2 J. Gunst, Yu. A. Litvinov, C. H. Keitel, and A. Pálffy, Phys. Rev. Lett. **112**, 082501 (2014).
3 F. Vagizov *et al.*, Nature **508**, 80 (2014); W. Liao *et al.*, Phys. Rev. Lett. **113**, 123602 (2014).
4 A. Politi, M. J. Cryan, J. G. Rarity, S. Yu, and J. L. O'Brien, Science **320**, 646 (2008).
5 Yu. V. Shvyd'ko *et al.*, Phys. Rev. Lett. **77**, 3232 (1999).

A Si-APD linear-array pixel detector for Nuclear Resonant Scattering measurements

S. Kishimoto, T. Mitsui,[1] R. Haruki, Y. Yoda,[2] S. Shimazaki,[3] M. Ikeno,[3] M. Saito,[3] and M. Tanaka[3].

Inst. of Materials Structure Science, KEK, 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan
[1]Kansai Photon Science Institute, JAEA, 1-1-1 Kouto, Sayo-cho, Hyogo 679-5198, Japan

[2]Japan Synchrotron Radiation Research Institute, 1-1-1 Kouto, Sayo-cho, Hyogo 679-5198, Japan

[3]Inst. of Particle and Nuclear Physics, KEK, 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan

We developed an X-ray detector system using a 64-pixel silicon avalanche photodiode (Si-APD) linear array and fast pulse-counting electronics for multichannel scaling [1]. The Si-APD linear array consists of 64 pixels each 100 × 200 μm^2 in size, with a pixel pitch of 150 μm and depletion depth of 10 μm. Ultrafast ASIC amplifiers and FPGAs can record both the position and timing of X-rays arriving at each pixel of the linear array with one ns pulse-pair resolution. The detector measured nuclear resonant forward scattering on ^{57}Fe, which spatial resolution and detection efficiency were improved by inclining the detector. A new linear-array detector system is now prepared for 0.5 ns pulse-pair resolution and for 128 pixels. We will present some results with sub-nanosecond time resolution in the workshop.

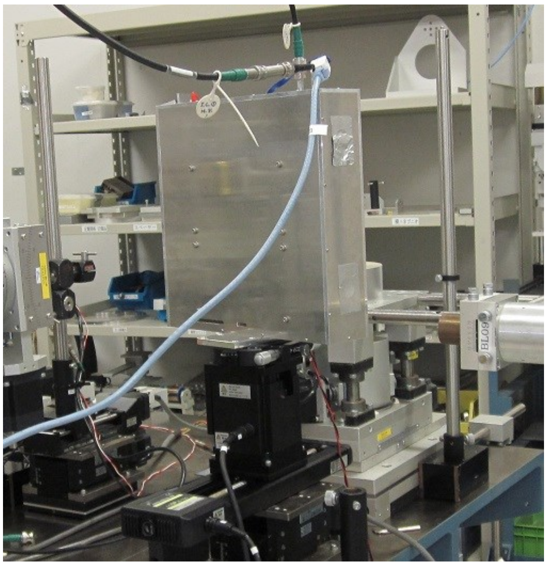


Figure 1: Photograph of the Si-APD linear-array detector.

References

[1] S. Kishimoto, T. Mitsui, R. Haruki, Y. Yoda, T. Taniguchi, S. Shimazaki, M. Ikeno, M. Saito, and M. Tanaka, Rev. Sci. Instrum. 85 (2014) 113102.

Improving Timing Performance in NRS Experiments by Utilizing a Fast 4 Channel TDC

O. Leupold, P. Alexeev, H.C. Wille, C. Strohm, M. Herlitschke, A.I. Chumakov[1], and R. Rüffer[1]

DESY, Notkestrasse 85, 22607 Hamburg, Germany
[1]ESRF, 71 Avenue des Martyrs. 38000 Grenoble, France

In nuclear resonant scattering (NRS) experiments the nuclear decay following the excitation of the sample by a strong synchrotron radiation (SR) pulse is monitored by fast detectors, usually avalanche photo diodes (APD). Combined with standard timing electronics based on NIM modules, time resolutions below 0.5ns can be achieved.

Standard NIM electronics has distinct disadvantages, which can be overcome by utilizing fast time to digital converters (TDC) for pulse detection, or even fast digitizers for fully resolved pulse shape and amplitude analysis. Here we present results obtained with a 4 channel TDC, MCS6A manufactured by FAST ComTec [1], which provides 100ps sampling time.

- In contrast to standard time amplitude converter (TAC) and ADC electronics the TDC can digest count rates up to 100 MHz, so no need anymore for blocking electronically the strong exiting pulse by a veto signal.
- The TDC has multihit capability, whereas the TAC/ADC can only register one delayed photon per exiting SR pulse. This is especially important for free electron laser sources.
- Due to its up to 5 input channels the MCS6A can measure the time spectrum for up to 5 detectors independently. Degrading performance of one detector during a measurement will not spoil the total measurent, as it is now the case.
- Due to the multihit capability he TDC can measure each bunch separately, whereas in nowadays electronics setup we average over all bunches.

Bunch purity is an important factor for a successful NRS experiment, especially at short nuclear life times NRS can suffer a lot from spurious bunches in a time interval up to ±16ns around the main bunch.

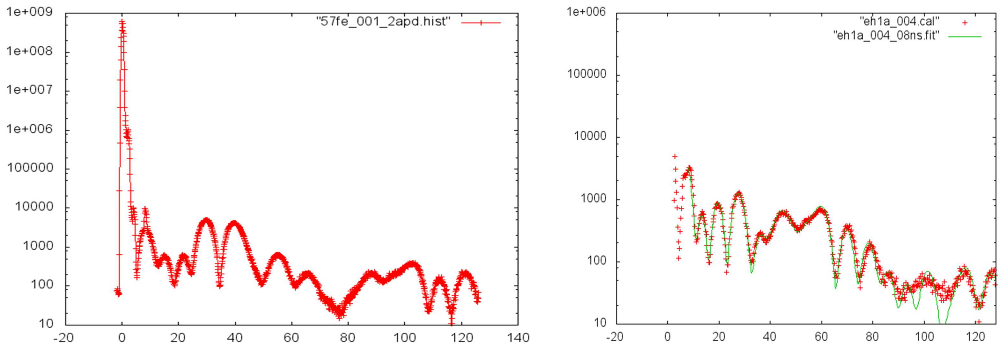


Figure 1 left: Time spectrum taken with TDC at P01/PETRA III in 60 bunch mode, including spurious bunch at 8ns. Right: Time spectrum taken with TAC/ADC at ID18/ESRF in hybrid bunch mode; the main bunch has to be electronically suppressed, the structure at about 8ns is an artifact from the gating electronics. A reasonable fit is only possible after about 10ns

References

1. http://www.fastcomtec.com/products/ultra-fast-multiscalers/mcs6a.html

Fast digitizers for fully time resolved nuclear resonant scattering applications

C. Strohm[1], P. Würtz[2], I. Sergeev[1], O. Leupold[1], H.-C. Wille[1], R. Röhlsberger[1], V. Schünemann[2], L. Dubrovinsky[3], A.I. Chumakov[4] and R. Rüffer[4]

[1]*Deutsches Elektronen Synchrotron, Notkestrasse 85, 22607 Hamburg, Germany*

[2]*Technische Universität Kaiserslautern, Erwin Schrödinger Strasse 46, 67663 Kaiserslautern, Germany*

[3]*Bayerisches Geoinstitut, Universitätsstrasse 30, 95447 Bayreuth, Germany*

[4]*European Synchrotron Radiation Facility, 71 Avenue des Martyrs, 38000 Grenoble, France*

Nuclear resonant scattering of synchrotron radiation is based on the time resolved detection of the nuclear decay on the scale of its lifetime after excitation with a pulsed synchrotron source. Currently, the detection relies on timing a single event per bunch spacing with respect to the last excitation, and time spectra are obtained through histogramming in multi channel analyzers [1]. The present scheme has a number of inherent limitations: pile up of several simultaneous or closely spaced pulses cannot be discriminated, only one event can be timed per excitation, the absolute time of the events is lost, and there is no information on the actual pulse height. The system is limited in both, burst and average rates.

In this contribution, we discuss the use of fast digitizers to implement time to digital converters for nuclear resonant scattering applications. Peak detection, deconvolution, and fitting procedures implemented in onboard field programmable gate arrays (FPGA) are expected to overcome the aforementioned limitations.

Analysis of the instrumental function of the detectors will allow to count simultaneous events correctly, improve the time resolution and separate different photon energies.

The separation of closely spaced events is key to accessing isotopes with short lifetimes.

The detection of multiple events per excitation is of particular importance with the advent of free electron laser sources in the hard x-ray regime, where multi photon excitations are expected.

Absolute timing with respect to external triggers, independent of the exciting synchrotron pulse, will enable pump probe experiments as for example pulsed laser heating in diamond anvil cells, laser excitation of spin transitions, photochemistry, or experiments in pulsed magnetic fields [2].

The combination of both, absolute timing and the ability to handle multiple events is the prerequisite for photon-photon statistics in the case of multi photon excitations [3] and experiments in nuclear quantum optics.

Energy analysis will allow to separate nuclear inelastic absorption at resonant and fluorescence energies to identify different sites through their respective hyperfine interactions [4], while still taking advantage of the additional statistics through the detection of fluorescence.

In this contribution, we present different strategies for the data analysis in the onboard FPGA of fast digitizers, and give first application examples.

References

1. A.Q.R. Baron, Hyperfine Interactions **125,** 29 (2000).
2. C. Strohm, P. Van der Linden and R. Rüffer, Phys. Rev. Lett. **104**, 087601 (2010).
3. R.H. Dicke Phys. Rev. **93**, 99 (1954).
4. M. Seto et al., Phys. Rev. Lett. **91**, 185505 (2003).

Nuclear Resonant Scattering Beamline at SPring-8

- Present Status, Recent Activities and Future Plan -

Y. Yoda

Japan Synchrotron Radiation Research Institute/SPring-8, 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo, 679-5198, Japan

BL09XU is a nuclear resonant scattering beamline with a SPirng-8 standard undulator. NRVS and Mössbauer spectroscopy have been intensively used in the various fields of science such as biochemistry, nono science, functional electronic device and so on [1][2][3]. Energy domain Mössbauer spectroscopy has been applied by Prof. Seto's group especially to the high enegy nuclei such as Yb-174 and Ni-61. A 20 cm long sample holder in the cryostat has been prepared for the dilute Ni protein samples. The beamtime sharing with HAXPES experiments started in 2014.

In 2012, Prof. Cramer's group started NRVS at BL19LXU, which is a RIKEN SR Physics beamline with a 25 m long undulator. Its spectrum is shown in Fogure 2. BL19LXU has been partly opened for public users since 2014. SPring-8 has a plan upgrade to the ultra low emittance ring aiming in 2020. The plan could affect the time differential experiments including the NRS experiments.

Figure 1: 20 cm long sample holder for a Ni protein.

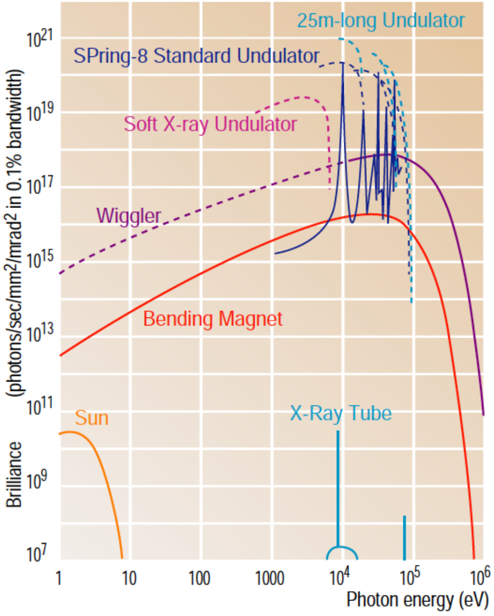


Figure 2: Spectra at SPring-8.

References

[1] H. Ogata, T. Krämer, H. Wang, D. Schilter, V. Pelmenschikov, M. van Gastel, F. Neese, T. B. Rauchfuss, L. B. Gee, A. D. Scott, Y. Yoda, Y. Tanaka, W. Lubitz and S. P. Cramer, Nature Comm., accepted.

[2] T. Nakano, N. Fukuda, M. Seto, Y. Kobayashi, R. Masuda, Y. Yoda, M. Mihara and Y. Nozue, Phys. Rev. B **91**, 140101(R) (2015).

[3] K. Hirai, D. Kan, N. Ichikawa, K. Mibu, Y. Yoda, M. Andreeva and Y. Shimakawa, Sci. Rep. **5**, 7894 (2015).

Synchrotron Mössbauer Source at ESRF: status report and applications

I. Kupenko, A.I. Chumakov, and R. Rüffer

ESRF-The European Synchrotron, CS40220,38043 Grenoble Cedex 9,France

We will present the status report on the Synchrotron Mössbauer Source at the Nuclear Resonance beamline at the ESRF[1]. We will discuss the current performance and present some recent results in various scientific fields.

References

[1] V. Potapkin, A. I. Chumakov, G. V Smirnov, J. P. Celse, R. Rüffer, C. McCammon, and L. Dubrovinsky, *J. Synchrotron Radiat.*, **19**, 4, 559, (2012).

Five years of Nuclear Resonant Scattering at the Dynamics Beamline P01 – results and future directions

H.-C. Wille, K. Schlage, P. Alexeev[1], L. Bocklage, L. Dzemiantsova, D. Erb, T. Guryeva,
I. Sergueev and R. Röhlsberger

Deutsches Elektronen-Synchrotron DESY, Notkestr. 85, D-22607 Hamburg, Germany
[1]Jülich Center for Neutron Science JCNS and Peter Grünberg Institut PGI, JARA-FIT, Forschungszentrum Jülich GmbH, DE-52425 Jülich, Germany

Five years ago the first nuclear resonant spectrum at the 6 GeV storage ring PETRA III has been recorded. The Nuclear Resonant Scattering (NRS) station at the Dynamics Beamline P01 is open for users since November 2011 [1]. We will demonstrate the new opportunities that a low emittance source offers for NRS studies by presenting some research highlights and instrument parameters. Namely, we report on the obersvation of electromagnetically induced transparency which opened the field of x-ray quantum optics at P01 [2]. In the following an experiment on the control of atomic coherences was performed [3] directly taking advantage of the low emmittance of the storage ring as the latter leads to an outstanding performance of a recently installed polarizer analyzer setup [4]. The excellent focussing capabilities at PETRA III were explored to perform *in situ* studies on nano samples during growth combining grazing incidence x-ray scattering and NRS (GINSAXS). This allows for determining the structure and magnetic properties of nano samples during growth. Furthermore, experiments on electron phonon coupling in high T super conductors under high pressure [5] and studies on spin waves in permalloy [6] will be discussed. In order to expand NRS to other isotopes a sapphire Bragg backscattering high resolution monochromator has been built and will be presented. A part of the presentation will dedicated to discuss the future research perspectives and experimental techniques to focus on with the user community.

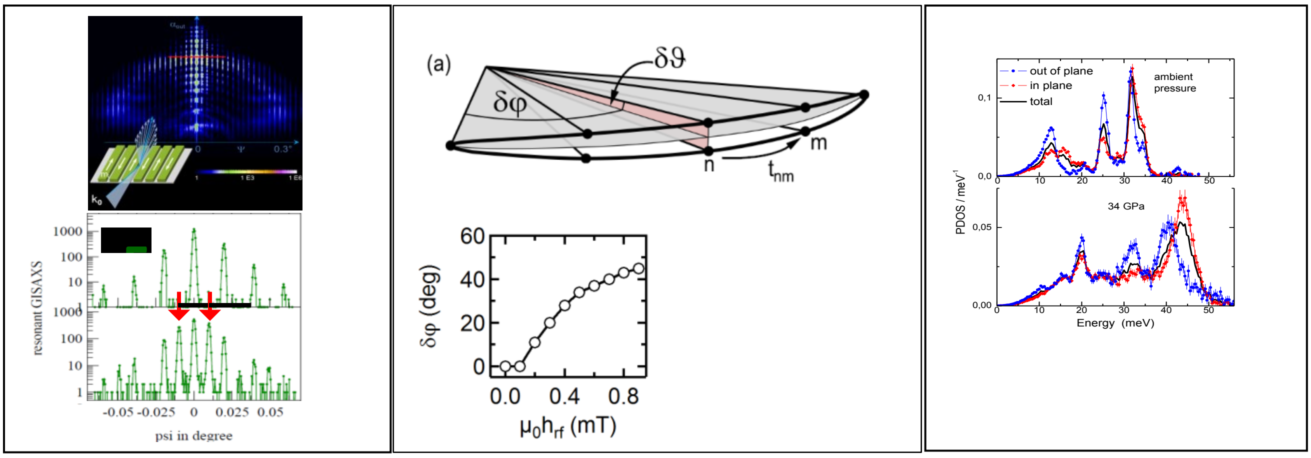


Fig. 1: GISAXS picture of thin magnetic the nano stripes (left upper part). Magnetic super structure Bragg peaks in the nuclear signal in ferro- and antiferromagnetic configuration (left lower part). Inplane and out of plane opening angles of a spin wave and the inplane dependance on the RF field amplitude determined by NRS (middle). Anisotropic vibrational dynamics of a Fe-As super conductor at ambient and at high pressure (right).

References

[1] http://photon-science.desy.de/facilities/petra_iii/beamlines/p01_dynamics/index_eng.html
[2] R. Röhlsberger et al., Nature 482, 199-203 (2012)
[3] K.P. Heeg et al., Phys. Rev. Lett., 111, 073601 (2013)
[4] B. Marx et al., Appl. Phys. Letters 105, 024103 (2014)
[5] I. Sergueev et al., to be published
[6] L. Bocklage et al., Phys. Rev. Lett. 114, 147601 (2015)

Sapphire Ultra Optics for Synchrotron Radiation

R. P. Hermann[1,@]

[1]Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA
[@]Former address: Jülich Centre for Neutron Science, Forschungszentrum Jülich GmbH, Jülich, Germany

A collaborative project involving the Shubnikov Institute for Crystallography of the Russian Academy of Science, the European Synchrotron Radiation Facility, the Karlsruhe Institute of Technology, Petra III at DESY and JCNS at Forschungszentrum Jülich was initiated in 2013 in the framework of a Helmholtz-Russia Joint Research Group "Sapphire Ultra Optics for Synchrotron Radiation". The goal of the collaboration is to overcome the challenges posed by nuclear resonance scattering (NRS) with ~1 meV energy resolution above 30 keV.

Sapphire has proven to be a material of choice for this task by enabling a dense choice of available energies in backscattering mode, providing a sufficient crystalline quality, and the possibility of energy control better than <0.1 meV. Between the first successful measurements of NRS for antimony-121[1-3] and the latest measurements with 1 meV resolution or better for tellurium-125 [4-6] and xenon-129 [7], 10 years have passed and most of the progress was achieved by improving the control of the optical elements [8]. It was also gradually recognized that defects are a major limiting factor and that a good knowledge of the defect structure of the specific used crystal is crucial. Eventually, a resolution better than 1 meV could be achieved at the 35.4 keV resonance of tellurium-125 and even high-pressure inelastic scattering [9] was possible. However, a better understanding and overcoming of the imperfection in the monochromator crystal remains essential.

The scope and progress of the work within the project that will be reviewed involves the growth and defect characterization of sapphire single crystals, the improvement and installation of a monochromator assembly at Petra III, the demonstration of improved resolution and access to resonance energies above 40 keV.

References

[1] Wille, H.-C. *et al. EPL* **74,** 170 (2006).

[2] Tsutsui, S. *et al. J. Phys. Soc. Jpn.* **76**, 065003 (2007).

[3] Wille, H.-C. *et al. Phys. Rev. B* **76,** 140301 (2007).

[4] Wille, H.-C. *et al. EPL* **91,** 62001 (2010).

[5] Matsunaga, T. *et al. Adv. Funct. Mater.* **21,** 2232 (2011).

[6] Bessas, D. *et al. Phys. Rev. B* **86,** 224301 (2012).

[7] Klobes, B., *EPL* **103,** 36001 (2013).

[8] Sergueev, I. *et al. J Synchrotron Radiation* **18,** 802 (2011).

[9] Simon, R. E. *et al. Semicond. Sci. Technol.* **29,** 124001 (2014).

Ways of obtaining low-dislocation sapphire crystals

A.N. Deryabin, A.V. Butashin, V.M. Kanevsky, and V.E.Asadchikov

A.V. Shubnikov Institute of Crystallography, Russian Academy of Sciences, Moscow, Russia

Sapphire crystals seem to be advanced reflecting material for the X-ray backscattering monochromators with energy of ~24 keV. In our preliminary experiments they were found the samples with acceptably low (<2 meV) half-width of the Bragg reflection line among the collection of the 15 samples, fabricated from the crystals grown by different techniques (the Verneuil, Czochralsky, Kiropoulos, HEM, and Bagdasarov). According to our preliminary analysis a value of this reflection line half-width is correlated with the dislocation density in sample. In the best samples, obtained by the Kiropoulos technique (Fig. 1), dislocation density was found to be about 10^2 $см^{-2}$, but in other samples this value reached ~10^6 $см^{-2}$ [1]. Obviously to increase the sensitivity of the X-ray backscattering monochromators on the base of sapphire crystals it is required samples with lower dislocation density, and even non-dislocation samples.

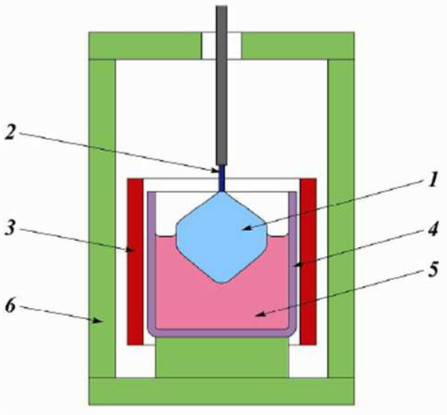


Fig. 1. Schematic unit for sapphire crystal growth by the Kiropoulos technique: 1 - growing crystal, 2 – seed, 3 – heater, 4 - crucible; 5 – melt, 6 – lining

To aim this goal we are improving the Kiropoulos technique, which is the mostly suitable to grow sapphire crystals of high quality. The main ideas of this improvement are following:

- to use the dislocation-free or low dislocation density seed;
- to apply “necking procedure” at initial stage of growth for decreasing the dislocation density in crystal;
- to build the “growing unit” with low value of temperature gradients in it (as low as ~$10 Kcm^{-1}$) to decrease thermoelastic stresses in crystal which promote to generation of new dislocation;
- to clean carefully the inner surface of the crucible to prevent the contamination of the alumina melt with refractory metal particles;
- to use the materials of the highest chemical purity as starting material (alumina) and as crucible, screens and heater materials (molybdenum, tungsten);
- to control carefully the crystal growth speed in the 0.5÷4 mm h^{-1} range to prevent the capture of the gas babbles, refractory metal particles by growing crystal and lineage formation in crystals (all of them promote to the dislocation generation).

References

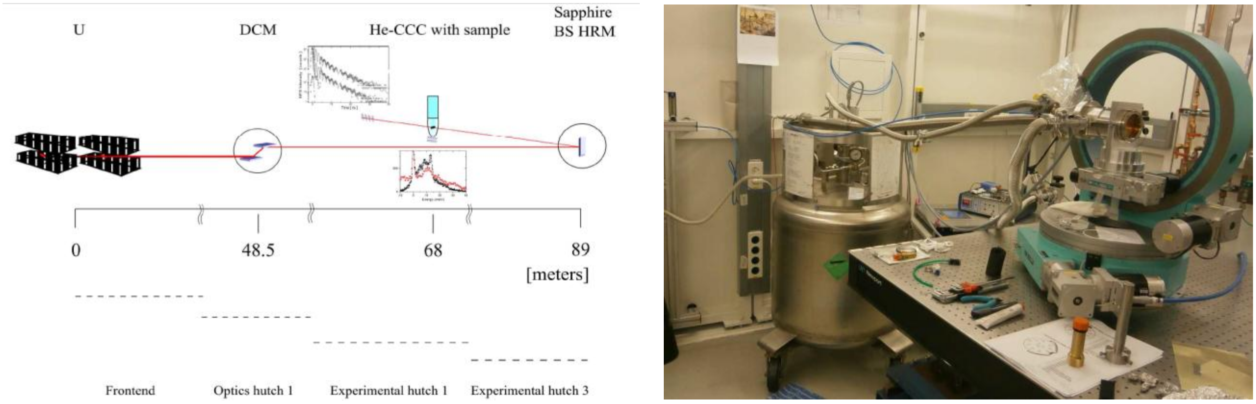
[1] V. Asadchikov, A. Butashin, A. Deryabin, et al. // 24-th ESRF Users Meeting, 3-5 February 2014, ESRF – Grenoble. Program, №86.

Sapphire backscattering monochromator at the Dynamics Beamline P01

P.Alexeev[1,4], V.Asadchikov[5], D.Bessas[2], A.Butashin[5], A.Cecilia[3], A.Chumakov[2], A.Deryabin[5], A.Ehnes[1], R.P.Hermann[4,6], A.Jafari[2,4,6], I.Prokhorov[5], R.Röhlsberger[1], B.Roshchin[5], R.Rüffer[2], K.Schlage[1], I.Sergeev[1], S.Stankov[3], H.-C.Wille[1]

[1]Deutsches Elektronen-Synchrotron, D-22607 Hamburg, Germany, [2]European Synchrotron Radiation Facility, F-38043 Grenoble, France, [3]Institute for Photon Science and Synchrotron Radiation, KIT, D-76344 Eggenstein-Leopoldshafen, Germany, [4]Jülich Centre for Neutron Science JCNS and Peter Grünberg Institut PGI, JARA-FIT, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany, [5]A.V. Shubnikov Institute of Crystallography, Russian Academy of Sciences, R-119333 Moscow, Russia, [6]Faculty of Sciences, University of Liège, B-4000 Liège, Belgium, [7]Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

We report on the sapphire backscattering high-resolution monochromator developed, installed and tested at the Dynamics Beamline P01 at PETRA III. The monochromator consists of a flow cryostat with sub-mK temperature stability hosting a high-quality sapphire crystal [1,2]. The efficiency of the monochromator was tested with nuclear resonance scattering on ^{119}Sn at 23.88 keV. An energy resolution of 1.4 meV and spectral reflectivity 35% were obtained. The monochromator provides access for hyperfine and phonon spectroscopy on Mössbauer isotopes with transition energies from 20 to 50 keV, e.g., ^{151}Eu at 21.5 keV, ^{125}Te at 35.5 keV, ^{121}Sb at 37.1 keV ^{129}Xe at 39.6 keV [3,4].



(a) (b)

Figure 1: Setup of BS HRM: (a) optical scheme, (b) photo of setup

References

[1] Yu. V. Shvyd'ko, X-Ray Optics, Springer Ser. Optical Science, Volume **98** (2004)
[2] M. Lucht, M. Lerche, H.-C. Wille et al., J. Appl. Cryst. **36**, 1075 (2003)
[3] I. Sergueev, H.-C. Wille, R.P. Hermann et al., J. Synch. Rad. **18**, 802 (2011)
[4] B. Klobes, A. Desmedt, I. Sergueev et al., Europhys. Lett., **103**, 36001 (2013)

Relationship Between Atomic Structure and the Roughness of Supersmooth Crystal Surface

A.V. Butashin, A.E. Muslimov, V.M. Kanevsky, A.N. Deryabin, B.S. Roshchin and V. E. Asadchikov

Shubnikov Institute of Crystallography, Russian Academy of Sciences, Leninskii pr. 59, Moscow, 119333 Russia

Technological advances in processing crystals (Si, sapphire α-Al_2O_3, SiC, GaN, $LiNbO_3$, $SrTiO_3$, etc.) of substrate materials and X-ray optics elements make it possible to obtain supersmooth surfaces with a periodicity characteristic of the crystal structure. These periodic structures are formed by atomically smooth terraces and steps of nano- and subnanometer sizes, respectively. A model surface with such nanostructures is proposed, and the relations between its roughness parameters and the height of atomic steps are determined. The roughness parameters calculated from these relations almost coincide with the experimental atomic force microscopy (AFM) data obtained from 1×1 and 10×10 μm areas on the surface of sapphire plates with steps. The minimum roughness parameters for vicinal crystal surfaces, which are due to the structural contribution, are calculated based on the approach proposed. A comparative analysis of the relief and roughness parameters of sapphire plate surfaces with different degrees of polishing is performed. A size effect is established: the relief height distribution changes from stochastic to regular with a decrease in the surface roughness.

High Precision X-ray Polarimetry – a powerful tool for nuclear resonant X-ray scattering

H. Bernhardt[1,2], *H.-C. Wille*[3], *L. Bocklage*[3], *J. Haber*[3], *K. Schlage*[3], *I. Uschmann*[1,2], *B. Marx-Glowna*[2], *K. S. Schulze*[1,2], *R. Loetzsch*[2], *E. Förster*[1,2], *T. Stöhlker*[1], *G. G. Paulus*[1,2], *R. Röhlsberger*[3]

[1] *Helmholtz Institute Jena, Fröbelstieg 3, 07743 Jena, Germany*
[2] *Institute for Optics and Quantum Electronics Jena, Max-Wien-Platz 1, 07743 Jena, Germany*
[3] *Deutsches Elektronen-Synchrotron DESY, Notkestraße 85, 22607 Hamburg, Germany*

We report on the application of high-purity x-ray polarimetry to study nuclear resonant scattering. Silicon channel-cut crystals were developed by a special procedure including crystal orientation, sawing and sophisticated edging methods. By using four to eight reflections per channel-cut the highest polarisation purity ($2.4\cdot10^{-10}$) measured in x-rays to date has been achieved [1]. The measurements were performed by combining a brilliant undulator source with an x-ray polarimeter based on multiple Bragg reflections at scattering angles very close to $2\theta=90^{\circ}$, i.e. a direct derivative of the scheme used by Barkla in 1903 to demonstrate the electromagnetic nature of x-rays. The best polarization purity was obtained at a photon energy of 6457 eV and constitutes an improvement of more than two orders of magnitude over all previously reported values. Our polarimeter has enough efficiency to measure the x-ray flux over 10 orders of magnitude within a reasonable time.

For the application of polarimetry in nuclear resonant scattering, the resonantly scattered photons can be discriminated against the photons emitted from the undulator source, due to their different polarization state that originates from optical anisotropies induced by nuclear hyperfine interactions [2]. Because the nonresonant photons of the source can be attenuated by more than nine orders of magnitude, time spectra as well as Mössbauer-spectra can be recorded without any temporal discrimination [3]. Those experiments were typically performed at photon energies of 14.4 keV using the silicon (840) reflection to excite the ^{57}Fe resonance.

In order to use other nuclear transitions, silicon channel-cuts with other reflections or different crystals will be used such that Bragg angles very close to 45° are achieved. In addition, we developed quasi channel-cut mounts to use two single crystals as “channel-cut”. This enables us to use different crystal materials such as diamond and quartz for high-purity x-ray polarimetry. Furthermore sophisticated crystal surface treatment will improve the polarization purity especially for coherent sources like X-ray free electron lasers.

References

[1] B. Marx, K. S. Schulze, I. Uschmann, T. Kämpfer, R. Lötzsch, O. Wehrhan, W. Wagner, C. Detlefs, T. Roth, J. Härtwig, E. Förster, T. Stöhlker and G. G. Paulus, *Phys. Rev. Lett.* **110**, 254801 (2013)

[2] E.E. Alp, W. Sturhahn and T.S. Toellner, *Hyperfine Interactions* **125**, 45 (2000)

[3] K. P. Heeg, H.-C. Wille, K. Schlage, T. Guryeva, D. Schumacher, I. Uschmann, K. S. Schulze, B. Marx, T. Kämpfer, G. G. Paulus, R. Röhlsberger, and J. Evers, *Phys. Rev. Lett.* **111**, 073601 (2013)

^{61}Ni Synchrotron Radiation Based Mössbauer Spectroscopy

R. Masuda, Y. Kobayashi, M. Saito, M. Kurokuzu, S. Kitao, T. Mitsui[1]*, Y. Yoda*[2]*, K. Hosoi*[3]*, H. Kobayashi*[3]*, H. Kitagawa*[3]*, and M. Seto*

Research Reactor Institute, Kyoto University, Kumatori-cho, Sennan-gun, Osaka, Japan
[1]*Condensed Matter Science Division, Japan Atomic Energy Agency, Sayo-cho, Sayo-gun, Hyogo, Japan*
[2]*Utilization Division, Japan Synchrotron Radiation Research Institute, Sayo-cho, Sayo-gun, Hyogo, Japan*
[3]*Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto, Japan*

Nickel compounds are important in many fields including materials science and industrial applications. Fortunately, we can study the nickel compounds by Mössbauer spectroscopy with ^{61}Ni nuclides [1]. However, it is by far less common than ^{57}Fe Mössbauer spectroscopy, because the radioactive isotope (RI) sources for it are not purchased and we must make the source using an accelerator. Same as other nuclides, synchrotron radiation (SR) is alternative source for ^{61}Ni Mössbauer spectroscopy. One difficulty in the SR measurement is low detection efficiency of the avalanche photo diode detector (APD), which enables fast time response and high dynamic range necessary for the detection of nuclear resonant scattering of SR. The first SR measurement was performed using nuclear resonant forward scattering (NFS) of ^{61}Ni-enriched Ni metal [2]. It overcomes the low detection efficiency by the optimum arrangement of the multi-element APD. Another candidate is SR-based Mössbauer spectroscopy [3]. The SR-based Mössbauer spectrum of ^{61}Ni-enriched Ni-doped superconductor was observed with a plastic scintillator for high energy X-rays [4]. In that experiment, the 67.4-keV direct scattered X-rays were detected, while internal conversion (IC) electrons were not. Now we applied the newly developed SR-based Mössbauer measurement system where the IC electrons are detected [5], to the ^{61}Ni Mössbauer spectroscopy. Although the IC coefficient of ^{61}Ni is 0.14 and it does not look efficient to detect the IC electrons, enhanced counting rate is obtained by the system and the natural Ni metal spectrum is obtained in 20 hours (Fig. 1). Although it still takes longer measuring time than the excellently efficient NFS, the applicability of natural Ni compounds actually widens the variety of available samples, such as rare samples and industrial materials.

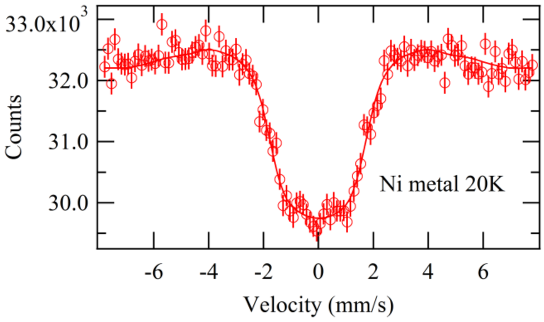


Figure 1: SR-based Mössbauer spectrum of non-enriched Ni metal.

References

[1] F. E. Obenshain and H. H. F. Wegener, Phys. Rev. **121** 1344 (1961).
[2] I. Sergeev, A. I. Chumakov, T. H. Deschaux Beaume-Dang, R. Rüffer, C. Strohm, and U. van Bürck, Phys. Rev. Lett. **99** 097601 (2007).
[3] M. Seto, R. Masuda, S. Higashitaniguchi, S. Kitao, Y. Kobayashi, C. Inaba, T. Mitsui, and Y. Yoda, Phys. Rev. Lett. **102** 217602 (2009).
[4] S. Kishimoto, F. Nishikido, R. Haruki, K. Shibuya, and M. Koshimizu, Hyperfine Interact. **204** 101 (2012).
[5] R. Masuda, Y. Kobayashi, S. Kitao, M. Kurokuzu, M. Saito, Y. Yoda, T. Mitsui, F. Iga, and M. Seto, Appl. Phys. Lett. **104** 082411 (2014).

Structural studies of magnetically anisotropic polycristalline Fe/MgO films on GaAs

V.E. Asadchikov, W.Hansen[2], I.A. Karateev[1], D.A. Khmelenin, B. Langraf[2], L. Liefeith[2], A.D. Nuzhdin, B.S. Roshchin, T. Slobodskyy[2], R. Tholapi[2], A.L. Vasiliev[1] and Yu.O. Volkov

A.V. Shubnikov Institute of Crystallography Russian Academy of Sciences
[1] National Research Centre "Kurchatov Institute"
[2] Hamburg University, Institute of Solid State Physics and Nanostructure

One of fundamental problems in spintronics is an effective generation and manipulation of spin-polarized charge carriers in semiconductors [1]. The most natural approach to solve the problem of spin-density and/or spin-current generation in semiconductors relies on the injection of spin polarized electrons from a metallic ferromagnet into semiconductor layer or quantum well [2]. However, it is well known that the efficiency of such processes is usually very low in the case of simple ferromagnet/semiconductor heterojunctions [1]. The electrons injected to semiconductor from the ferromagnet do not preserve their spin orientation, and the main physical reason of this effect is the huge difference in conductivities of ferromagnetic metals and semiconductors [3].

It has been suggested [4], [5] that a thin tunnelling barrier separating semiconductor from metal can help injecting spin polarized current, because during the electron tunnelling through the barrier the spin orientation does not change, whereas the conductivity mismatch effect is absent in this case. MgO tunnelling barrier was reported to be promising for spin injection [6].

In regard to fabricate spin injection and detection devices it is important to achieve smooth interface morphologies of the embedded MgO film. Spin and charge transport properties of the obtained heterostuctures were reported in [7]. EDX image of heterostructure is shown on fig. 1.

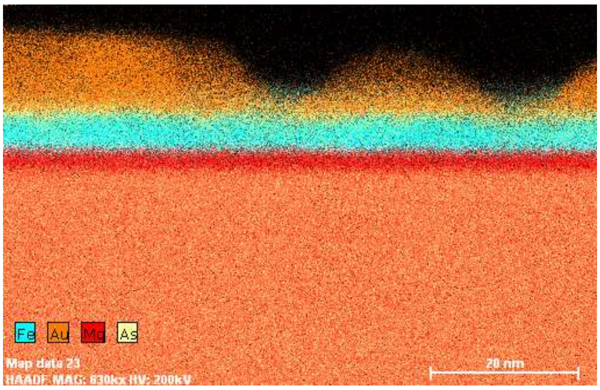


Figure 1: Energy dispersive X-ray spectroscopy of Au/Fe/MgO/GaAs heterostructure.

The results on TEM, HRXRD of MgO without Fe, XRR of Au/Fe/MgO/GaAs heterostructures will be presented as well as magnetic anisotropy studies.

References

[1] J. Fabian, A. Matos-Abiague, C. Ertle et al., Acta Physica Slovaca **57**, 565 (2007).
[2] G.-X. Miao, M. Münzenberg, and J. S. Moodera, Reports on Progress in Physics **74**, 036501 (2011).
[3] G. Schmidt, D. Ferrand, L.W. Molenkamp et al., Phys. Rev, B **62**, R4790 (2000).
[4] E.I. Rashba, Phys. Rev. B **62**, R16267 (2000).
[5] D.L. Smith and R.N. Silver, Phys. Rev. B **64**, 045323 (2001).
[6] X. Lou et al., Nat Phys **3**, 197 (2007).
[7] S. Wolski, T. Szczepanski, V.K. Dugaev et al., J. of Appl. Phys. **117**, 043908 (2015).

Setups for Synchrotron-Radiation Mössbauer Spectroscopy Using a Nuclear Bragg Monochromater at SPring-8 and Their Applications to Spintronics-Related Thin Films

K. Mibu

Graduate School of Engineering, Nagoya Institute of Technology, Nagoya, Aichi 466-8555, Japan

Recent development in synchrotron-radiation Mössbauer spectroscopy using a nuclear Bragg monochromater has made it possible to measure ^{57}Fe Mössbauer spectra in energy domains with a synchrotron source. This method is in a practical phase also for the studies on magnetic thin films, and experiments that have not been so easy with a conventional method using a radioisotope source and conversion electron detection have become easily performable [1]. The energy-domain measurements (in contrast to time-domain measurements) have made it easier to interpret the spectra of practical magnetic thin films, where nuclear environments are usually not so uniform.

In this presentation, the recent setups for synchrotron-radiation Mössbauer spectroscopy using a nuclear Bragg monochromater at the beamline BL11XU, SPring-8, are introduced briefly. Then, energy-domain experiments on spintronics-related thin films and phenomena, which contain those at low temperatures under external magnetic fields [2], those using a circularly polarized X-ray source [3], and those under an electric current flow [4], are demonstrated. Such experiments could be possible with the traditional method using a radioisotope source and conversion electron detection, but can be performed much effectively using synchrotron setups, which will be elaborated in the presentation.

These works were financially supported by Grants-in-Aid for Scientific Research (B) and (S) from Japan Society for the Promotion of Science (JSPS) and the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. The experiments were performed at the beamline BL11XU, SPring-8, in collaboration with Dr. T. Mitsui at JAEA, Dr. M. Seto and his team members at Kyoto University. The samples were prepared under the collaborations with Dr. M. A. Tanaka at Nagoya Institute of Technology and Dr. H. Yanagihara and Dr. E. Kita at University of Tsukuba.

References

[1] K. Mibu *et al.*, Hyp. Int. **217**, 127 (2013).
[2] K. Mibu *et al.*, ICAME2015 (2015).
[3] T. Mitsui *et al.*, J. Synchrotron Rad. **22**, 427 (2015).
[4] K. Mibu *et al.*, J. Appl. Phys. **117**, 17E126 (2015).

Perspectives for NRS on selected metalloproteins

M. Haumann

Freie Universität Berlin, Fachbereich Physik, Institut für Experimentalphysik, Arniamllee 14, 14195 Berlin, Germany

An estimated >50 % of all biological enzymes contain metal atoms as essential constituents of their active site. Particularly interesting are small-molecule converting enzymes, catalyzing for example hydrogen (H_2) or oxygen (O_2) activation reactions under ambient conditions (*1-6*). Important questions with respect to the catalytic mechanisms address molecular and electronic structures, as well as vibrational dynamics of the metal centers in reaction intermediates. X-ray based spectroscopy methods in principle can provide geometric parameters, electronic configurations, and vibrational modes of the metal-protein complexes. Highly interesting are nuclear resonance spectroscopy methods, which now are spreading due to recent technical developments at 3^{rd} or 4^{th} generation synchrotron radiation sources. Nuclear resonance vibrational spectroscopy (NRVS) on ^{57}Fe labelled enzymes probes vibrational modes of metal centers with unprecedented site selectivity. Nuclear forward scattering and synchrotron Mössbauer techniques complement conventional laboratory methods. Besides iron, also other elements (Ni, Te) are potentially interesting for NRS investigations on proteins. However, so far relatively few results using NRS on metalloproteins are available in the literature. This may be expected to change rapidly due to opening of new NRS beamlines and technical improvement at operating sources, as well as due to the numerous interesting biological systems that possibly can be studied by NRS techniques. On the other hand, there are challenges with respect to experimental approaches and interpretation of NRVS spectra. Significant progress in quantum chemical approaches such as density functional theory (DFT) now facilitates calculation of various X-ray spectroscopic signals (XAS, XES, NRS), but the quality of matching between experimental and theoretical data needs to be better defined for quantitative spectral interpretation. Typical questions for NRVS experiments on metalloproteins address metal redox and spin states, ligand binding and protonation states, and intermediate formation in the catalytic cycle. Examples of NRVS experiments and underlying questions on H_2 and O_2 converting enzymes from our work and from the literature will be described, possible problems with respect to experimental strategies and data evaluation are discussed, and a brief outlook on future perspectives of applying NRS techniques to metalloproteins is provided.

References

[1] K. Sigfridsson, N. Leidel, O. Sanganas, P. Chernev, O. Lenz, K. Yoon, H. Nishihara, A. Parkin, F. Armstrong, S. Dementin, M. Rousset, A. De Lacey, M. Haumann, Biochim Biophys Acta **1847**, 162 (2013).

[2] M. Haumann, in: Biohydrogen (M. Rögner, Ed.), DeGruyter, Berlin, 97-116 (2015)

[3] C. Lambertz, P. Chernev, K. Klingan, N. Leidel, K. Siegfridsson, T. Happe, M. Haumann, Chem. Sci. **5**, 1187 (2014).

[4] P. Chernev, C. Lambertz, A. Brunje, N. Leidel, K. Sigfridsson, R. Kositzki, C. Hsieh, S. Yao, R. Schiwon, M. Driess, C. Limberg, T. Happe, M. Haumann, Inorg Chem **53**, 12164 (2014).

[5] K. Sigfridsson, P. Chernev, N. Leidel, A. Popovic-Bijelic, A. Gräslund, M. Haumann, J Biol Chem **288**, 9648 (2013).

[6] N. Leidel, A. Popovic-Bijelic, K. Havelius, P. Chernev, N. Voevodskaya, A. Gräslund, M. Haumann, Biochim Biophys Acta **1817**, 430 (2012).

Nuclear Resonant Small-Angle Scattering:

Accessing the Spatial Spin-Distribution of Nanomaterials

M. Herlitschke[1], I. Sergeev[1], S. Disch[2], K. Schlage[1], E. Wetterskog[3], L. Bergström[3], M. Miglierini[4,5] and R. P. Hermann[6,7]

[1] FS-PE, Deutsches Elektronen-Synchrotron, 22607 Hamburg (Germany)
[2] Department Chemie, Universität zu Köln, 50939 Köln (Germany)
[3] Department of Materials and Environmental Chemistry, Stockholm University, 10691 Stockholm (Sweden)
[4] Institute of Nuclear and Physical Engineering, Slovak University of Technology, 81219 Bratislava (Slovakia)
[5] Regional Centre of Advanced Technologies and Materials, Palacky University, 77146 Olomouc (Czech Republic)
[6] JCNS-2 and PGI-4, JARA-FIT, Forschungszentrum Jülich GmbH, 52425 Jülich (Germany)
[7] Faculté des Sciences, Université de Liège, 4000 Liège (Belgium)

The investigation of the spatial spin-distribution in nanosized material is a challenging task of nowadays science [1, 2]. For structures with dimensions of only a few nanometers, some common measurement methods are limited due to the missing long range translation symmetry, the small sample amount, and the change of the spin order at the sub-nanometer scale.

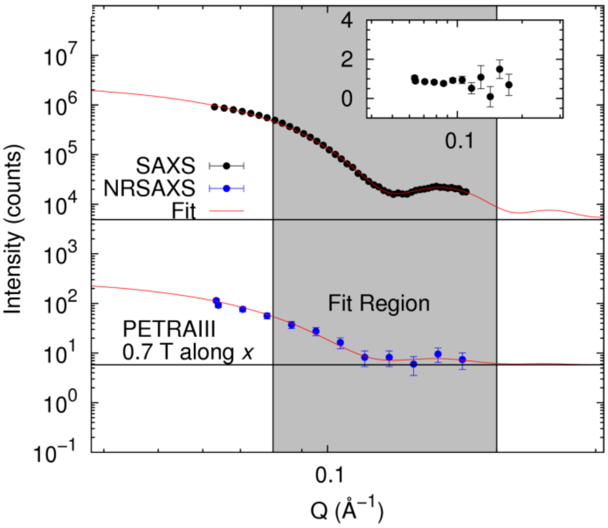


Fig. 1: Prompt (SAXS) and delayed (NRSAXS) scattering of nanospheres, fitted with a hard sphere form factor. Inset: NRSAXS/SAXS signal scaled by 10^4.

We aim for a new approach of nano-characterization through the combination of the two commonly used techniques for nanomaterials, Small-Angle X-ray Scattering (SAXS) and Nuclear Resonant Scattering (NRS). SAXS gives access to the spatial information of the material at the nanometer scale and NRS allows for studying the hyperfine field and thus indirectly the magnetism. The Nuclear Resonant Small-Angle X-ray Scattering (NRSAXS) technique has been already applied for characterizing domains in the micrometer regime in foils and thin layers [3,4].

We will present our results of the application of the iron-57 nuclear resonance to the small-angle scattering technique. In the presentation, a theoretical overview will be given on how the local variation of the magnetization can lead to nuclear resonant small-angle scattering. First experimental results of this technique, applied to nanoparticles in solution and a NANOPERM [5] material, will be discussed.

In such an experiment, the recorded data sets are the prompt scattering (SAXS) and the delayed scattering (NRSAXS), measured simultaneously (see Fig.1). As a result of this parallel measurement of both signals, deviations due to alignment, intensity and sample shape can be excluded and an analysis of very small difference in the resonant and non-resonant form factor is thus possible.

References

[1] S. Disch, *New Journal of Physics*, **14**, 013025 (2012)
[2] K. L. Krycka, *Phys. Rev. Lett.*, **104**, 207203 (2010)
[3] Y. V. Shvyd'ko, *Phys. Rev. B*, **54**, 14942–14945(1996)
[4] D. L. Nagy, *Phys. Rev. Lett.*, **88**, 157202 (2002)
[5] M. Miglierini, *Journal of Applied Physics*, **85**, 1014–1025 (1999)

Nuclear Resonance Scattering of Antimony Trioxides

A.Jafari[1,2,3], *R. E. Simon*[1,2], *A. Mahmoud*[1], *V. L. Deringer*[4], *R. P. Stoffel*[4], *R. Dronskowski*[4],

I. Sergeev[5], *D. Bessas*[3], *B. Klobes*[1] *and R.P. Hermann*[1,6]

[1] *Jülich Centre for Neutron Science JCNS and Peter Grünberg Institute PGI, Forschungszentrum Jülich, Jülich, Germany*
[2] *Faculty of Sciences, University of Liège, Liège, Belgium*
[3] *European Synchrotron Radiation Facility, Grenoble, France*
[4] *Institute of Inorganic Chemistry, RWTH Aachen University Landoltweg 1, Aachen*
[5] *Deutsches Elektronen-Synchrotron, Hamburg, Germany*
[6] *Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*

The lattices dynamics of the α-, β-Sb_2O_3 and α-TeO_2 have been carried using nuclear inelastic and nuclear forward-scattering. Experimentally obtained density of phonon states were found to be comparable with calculations based on density functional theory. Moreover, the vibrational frequencies were compared with several reports and some modes observed for first times [1-3]. Hyperfine parameters of α- and β-Sb_2O_3 obtained using Mössbauer spectroscopy and nuclear forward scattering. Pronounced quadrupole splitting ~ 9 mm/s for both Sb oxides that is correlated to lone-pair electrons of Sb. The calculated Debye temperature of 201(3) K from temperature dependence Mössbauer spectroscopy measurements agrees well with 208(8) K extracted from DPS.

References

[1] C. A. Cody, L. Dicarlo, and R. K. Darlington, Inorg Chem **18**, 1572 (1979).

[2] A. E. Whitten, B. Dittrich, M. A. Spackman, P. Turner, and T. C. Brown, Dalton Transactions, **23** (2004).

[3] A. L. J. Pereira, L. Gracia, D. Santamaria-Perez, R. Vilaplana, F. J. Manjon, D. Errandonea, M. Nalin, and A. Beltran, Phys Rev B **85** (2012).

A New Class of Layered Materials with Freely Adjustable Novel Spin Profiles for Precision Spintronics

Kai Schlage[1], Lars Bocklage[1,2], Denise Erb[1], Hans-Christian Wille[1], and Ralf Röhlsberger[1,2*]*

[1]Deutsches Elektronen-Synchrotron DESY, Notkestrasse 85, 22607 Hamburg, Germany
[2]The Hamburg Centre for Ultrafast Imaging, Luruper Chaussee 149, 22761 Hamburg, Germany

Next information and sensor technology is based on progress in spintronic multilayer design. The interlayer coupling approach used to engineer the magnetization profiles in these systems imposes fundamental limitations on the adjustability of their magneto-electronic response. We demonstrate that oblique incidence deposition (OID) can be used in a facile way to freely adjust the magneto-electronic properties in ultra-thin multilayer devices made from any magnetic material, with any non-magnetic spacer layer.

The functionality of these devices is not based on interlayer coupling but solely depends on the magnetic anisotropy of the individual layers. In this new class of layered materials crossed multilayer easy axes with adjustable opening angle *(Fig. 1)* and custom-made switching fields of the individual layers can be precisely realized for the first time. Low and high-field magneto-electronic multilayers and spin-valve systems with tailor-made magneto-resistive functionality can be fabricated in a simple fashion from the same type of multilayer systems (identical layer structure and chemical composition) by adjusting the magnetic properties via oblique incidence deposition.

Irrespective of the interface roughness that goes along with the deposition via OID a very clean and strong magneto-resistive signal is obtained in in ferromagnetic/nonmagnetic/ferromagnetic building trilayers that multiplies by simple stacking of such building blocks. Thus new routes are opened up for magnetic multilayer design, and the functionality of spintronic devices can be adjusted to particular applications with unprecedented accuracy [1].

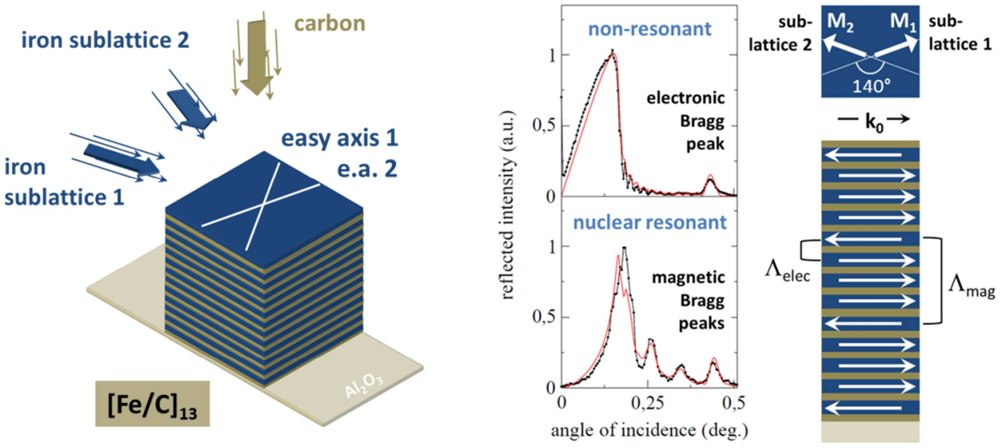


Figure 1: Novel spin arrangement in a $[Fe/C]_{13}$ multilayer demonstrating the versatile tuning possibilities of oblique incidence deposition. The sequence of azimuthal deposition angles α for subsequent Fe layers (α = +20°, -20°, -20°, -20°) results in a magnetic ground state in which the vertical magnetic correlation length (Λmag) is four time the structural one Λelec , as evidenced by the magnetic Bragg peaks in the resonant x-ray reflectivity curve. The red curves are simulations for the layer profile shown on the right.

References

[1] K. Schlage, D. Erb, R. Röhlsberger, H.-C. Wille, L. Bocklage, D. Schumacher. Method of producing a multilayer magnetoelectronic device and magnetoelectronic device. EP13183166 (2014)

Mössbauer Studies of Europium under Extreme Pressures

Wenli Bi,[1] Jinhyuk Lim,[2] Gilberto Fabbris, [1,2] Jiyong Zhao,[1] Daniel Haskel,[1] Ercan E. Alp,[1]
Michael Y. Hu,[1] and James S. Schilling[2]

[1]Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439, USA
[2]Department of Physics, Washington University, St. Louis, MO 63130, USA

Eu, as a mid-member of lanthanide metals, is divalent and has strong local magnetic moment with seven $4f^7$ electron (J=7/2). At ambient pressure Eu orders antiferromagnetically below 90 K [1, 2]. It has been predicted that under significantly high pressure Eu may lose one 4f electron and become trivalent and nonmagnetic ($4f^6$, J=0), and possibly superconducting [3]. Indeed with pressure above 80 GPa, Eu was found to be superconducting with $T_c \sim 2$ K [4]. To understand the superconductivity, valence and magnetism in Eu have been studied under pressure up to 1 Mbar using synchrotron Mössbauer spectroscopy. The hyperfine parameters change drastically with increasing pressure. Combining the changes of isomer shift (see Figure 1) with DFT calculations, x-ray absorption, and x-ray emission experiments, we have shown that Eu remains divalent up to 119 GPa, contrary to the previous report that Eu becomes mixed valent at pressures below 10 GPa [5-7]. At 11 K with increasing pressure, the magnetic hyperfine field (H_{hf}) increases to 60 T from 26.5 T at ambient pressure. While further pressure is applied, Eu's magnetism starts to collapse above 81 GPa, coinciding with the emergence of superconductivity above 80 GPa (Figure 2). These results reveal that extreme pressure drives Eu into an unusual ground state with coexistence of superconductivity and strong local magnetic moment.

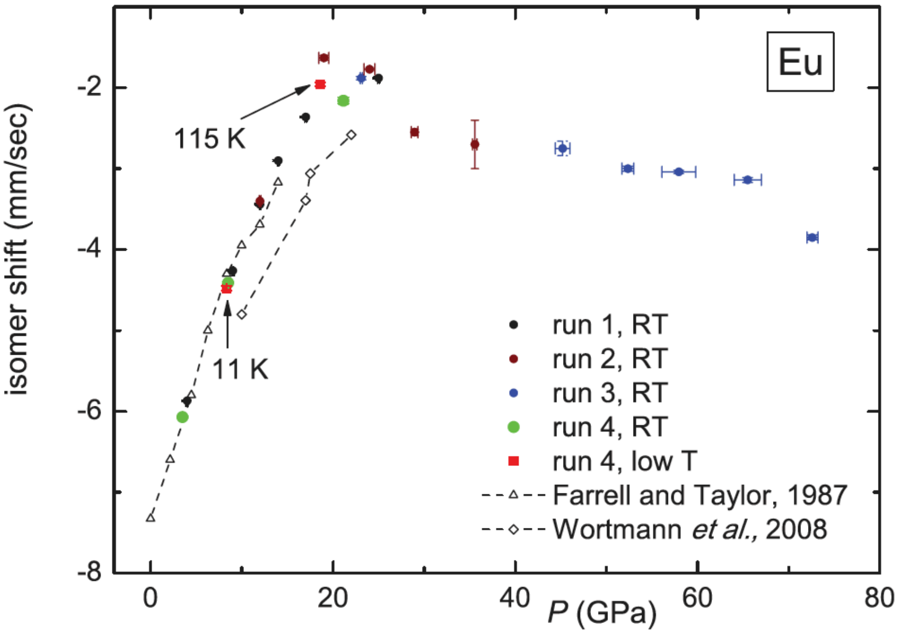


Figure 1: Isomer shift of Eu under pressure in comparison with previous studies.

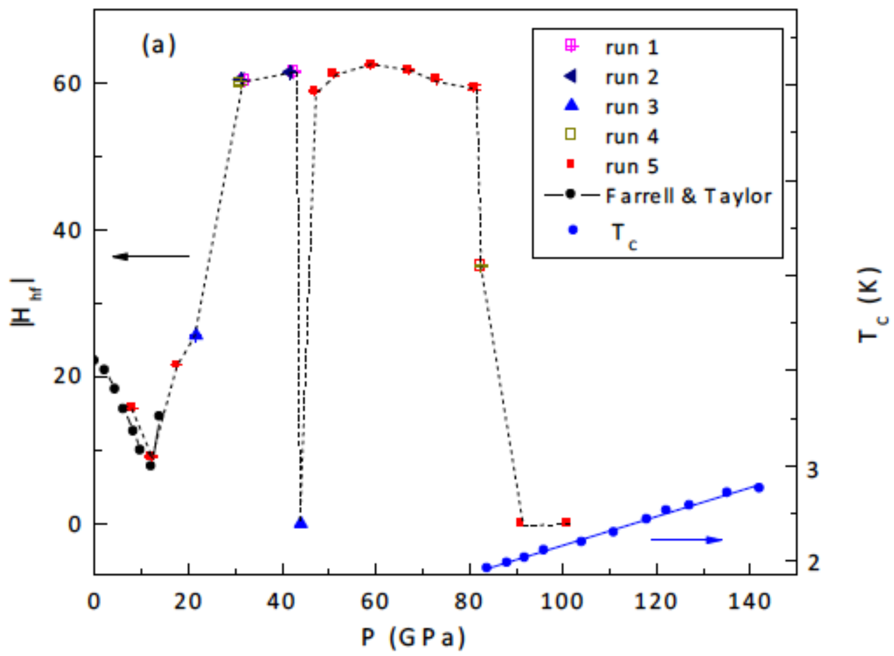


Figure 2. Magnetic hyperfine field versus pressure up to 1 Mbar. Superconducting transition temperatures T_c versus pressure are also included to show that the collapse of magnetism coincides with the emergence of superconductivity above 80 GPa.

References

[1] P. Barrett and D. Shirley, Phys. Rev. **131**, 123 (1963).

[2] R. Cohen, S. Hüfner, and K. West, Phys. Rev. **184**, 263 (1969).

[3] B. Johansson and A. Rosengren, Phys. Rev. B **11**, 2836 (1975).

[4] M. Debessai, T. Matsuoka, J. Hamlin, J. S. Schilling, and K. Shimizu, Phys. Rev. Lett. **102**, 197002 (2009).

[5] J. Rŏhler, Physica (Amsterdam) 144B, 27 (1986).

[6] J. Farrell and R. Taylor, Phys. Rev. Lett. 58 , 2478 (1987).

[7] G.Wortmann, U. Ponkratz, B. Bielemeier, and K. Rupprecht, High Press. Res. 28, 545 (2008).

NFS Experimental Data Transformation from Time to Energy Domain

V. Procházka, P. Šretrová, V. Vrba, and M. Miglierini[1]

Faculty of Science, Palacky University, 771 46 Olomouc, Czech Republic

[1]Institute of Nuclear and Physical Engineering, Slovak University of Technology, 812 19 Bratislava, Slovakia

Evaluation procedure of Nuclear forward scattering (NFS) experiments is based on a fitting procedure of the measured NFS interferograms by theoretical curves which are calculated according to a physical model using selected set of hyperfine parameters. This fitting process is usually accomplished via appropriate software packages, e.g. CONUSS [1], MOTIF [2]. Success of the evaluation procedure depends on whether the physical model consists of appropriate spectral components and on a good choice of starting values of the fitted parameters. In case of a classical Mössbauer spectroscopy measured in energy domain using vibrating radioactive source, the choice of a physical model is obvious since we can directly observe the transitions between nuclear levels. Nevertheless, in case of NFS the choice of proper components in a physical model is more complicated as we observe Fourier picture of the nuclear transitions. This situation is comparable to X-ray diffraction experiments used for determination of crystalline structure. The picture of a crystal structure is observed in reciprocal space and direct transformation to real space using Fourier transform is not possible due to the phase problem. We can avoid this using iterative process where the missing phase is calculated according to a physical model or similar structures already solved. Later on it is refined iteratively by applying constrains on the resulting electron density.

The possibility of transformation of NFS interferograms into energetic domain is discussed. This procedure can not replace the fitting in time domain but it can be useful for constructing an appropriate physical model for such fitting procedure. NFS is a useful technique for in-situ observation of chemical or physical processes, e.g. crystallization and/or progress of chemical reactions. The typical task that can be solved using NFS is observation of intermediate state formation. Nevertheless, such an analysis is complicated in two aspects. First, the amounts of the intermediate states are usually relatively small. Second, it is a serious problem to guess hyperfine parameters of the intermediates when we can observe only interferogram in time domain. Here, the signal of each spectral component is spread out over the whole measured range while in energy domain the signal is concentrated into a narrow energy range. Using transformation of interferograms into energy domain we should be able to identify the energy range where the fitting does not correspond with the suggested theoretical model. Possible solutions are suggested and the weak points of this transformation will be discussed including constrains for Mössbauer spectra.

References

[1] W. Sturhahn, E. Gerdau, Phys. Rev. B 49 (1994) 9285.

[2] Yuri V. Shvyd'ko, Hyperfine Interactions 125 (2000) 173–188.

Transverse coherence of synchrotron beam and reflectivity data interpretation for magnetic multilayers

M.A. Andreeva

Faculty of Physics, M.V. Lomonosov Moscow State University, 119991 Moscow, Russia

The nuclear resonance reflectivity (NRR) measurements provide us with an excusive depth-resolved information about the magnetization ordering in multilayers. In the most NRR experiments the data are treated in terms of the definite magnetization azimuth angle for each magnetic sublayer in multilayer (e.g. [1-4]). Herewith it is covertly implied that each sublayer is magnetically homogeneous along the surface. But it is obvious and nowadays experimentally well proved that even ultrathin magnetic layers have domain structure up to magnetization saturation. If the beam spot on the surface is much larger than the average domain size and the scattering amplitudes from different domains are fully coherent we should get the pattern of random in plane distribution of hyperfine fields. However it is not the case (see e.g. [1]).

The new idea, which we now develop, is the necessity to take into account the finite transverse coherence length of synchrotron beam [5-6] which is essential for the large illuminated areas on the surface at grazing incidence. In this case the interference from different domains is partially suppressed by the factor C_{coh} ($0 \le C_{coh} \le 1; C_{coh} = 1$ for fully coherent case). For σ- polarized SR (π- polarized magnetic field of radiation and hereinafter we work with the polarization of the magnetic field of radiation) the domains with different azimuth orientations of magnetization give the reflected waves of σ- and π- polarizations having different quantum beats in the $f_\pi(t)$ and $f_\sigma(t)$ decay dependences. It can be shown that in the kinematical approximation of the reflectivity theory $f_\pi(t)$ dependences are the same for all orientations of magnetizations but $f_\sigma(t)$ have the opposite sign for the inverse magnetization orientations along the beam direction. If the domain magnetizations have random orientations we can easily derive for the reflectivity intensity:

$$I_R(t) \propto (1+3C_{coh})\left|f_\pi(t)\right|^2 + \frac{1}{2}(1-C_{coh})\left|f_\sigma(t)\right|^2 . \qquad (1)$$

That means that for the fully coherent beam we have no σ- polarized contribution but for partially coherent case we have it. It looks like the magnetization in our sample have definite azimuth angle γ^{eff} when the reflectivity intensity is described by the formula

$$I_R(t) \propto \left|f_\pi(t)\right|^2 + \sin^2\gamma^{eff}\left|f_\sigma(t)\right|^2 \qquad (2)$$

By comparison of (1) and (2) we have got the formula which connects the obtained "effective" azimuth angle γ^{eff} with the transverse coherence length of the synchrotron beam [5] in units of the average domain size. The separation of the "effective" azimuth angle onto the real magnetization direction and the part, stipulated by the partial coherence of the waves scattered be different domains, can be achieved by the measurements for different sample orientations. The difference of the magnetization directions obtained at two sample orientations opens a way for determination of the transverse coherence length of the synchrotron beam if the domain size is known and vice-versa: the average domain size can be evaluated if the coherence length is known.

References

[1] M.A. Andreeva, V.G. Semenov, L. Häggström, et al., Hyperfine interactions **136/137**, 687 (2001).

[2] C. L'abbe´, J. Meersschaut, W. Sturhahn, et al., Phys. Rev. Let. **93**, 037201-1 (2004).

[3] T. Diederich, S. Couet, and R. Röhlsberger, Phys. Rev. B **76**, 054401 (2007).

[4] T. Ślęzak, M. Ślęzak, M. Zając, et al., Phys. Rev. Lett. **105**, 027206 (2010).

[5] A.Q.L. Baron, Hyperfine Interactions **123/124**, 667 (1999).

Nuclear resonance reflectivity investigation of the field induced magnetization reorientation in antiferromagnetic [Fe/Cr]$_n$ multilayers

M. Andreeva, A. Gupta[1], G. Sharma[2], S. Kamali[3], K. Okada[4], and Y. Yoda[4]

Faculty of Physics, M.V. Lomonosov Moscow State University, 119991 Moscow, Russia
[1]Indore Center, UGC-DAE Consortium for Scientific Research, Indore 452017, India
[2]Center for Spintronic Materials, Amity University UP, Noida 201313, India
[3]Department of Applied Science, University of California, Davis, California 95616, USA
[4]Japan Synchrotron Radiation Research Institute, SPring-8, Sayo, Hyogo 679-5198, Japan

Extensive investigation of the magnetization reversal in the [^{57}Fe (3.0 nm)/Cr (1.2 nm)]$_{10}$ ML having the antiferromagnetic interlayer coupling under the action of the applied magnetic field have been performed at the station BL09XU of SPring-8. Angular dependences of the nuclear resonance reflectivity (NRR) and the time spectra at Bragg angles of different orders have been measured for different magnitudes of the gradually increased external field (0 – 1500 Oe) applied perpendicular (T-geometry) and along (L-geometry) the beam direction (see e.g. Fig. 1). The joint fit of the whole set of the data for each value of the external field performed by the REFTIM package [1] gives the noncollinear twisted magnetization depth-profiles where the spin flop state appears sequentially in different ^{57}Fe layers at increasing applied field. The result partially confirms the theoretical predictions [2] but in our case we see that the magnetization reorientation starts not only from the top and bottom layers and the spin-flop event appears initially in the center of ML.

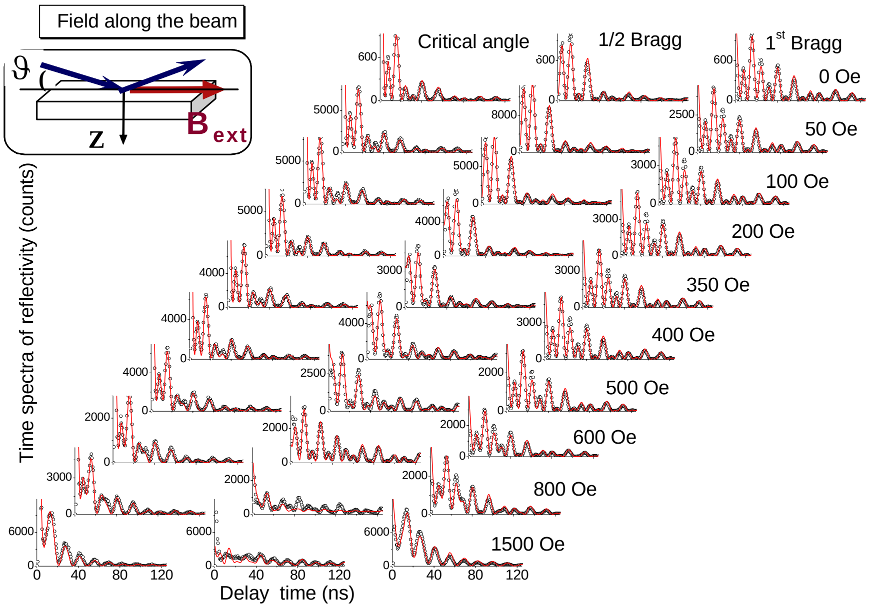


Figure 1: Time spectra of NRR reflectivity, measured at three incidence angles of SR for different magnitude of the ascending external field in L-geometry. Symbols represent the experimental data, lines – fit results.

The support through SERB grant SB/S2/CMP-007/2013 and through RFBR grants No. 09-02-01293-a and No. 15-02-01502-a is thankfully acknowledged. The synchrotron radiation experiments were performed at SPring-8 with the approval of JASRI (Proposal No. 2010B1298).

References

[1] M.A. Andreeva, Hyperfine Interactions **185**, 17 (2008).
[2] J. Meersschaut, C. L'abbé, F. M. Almeida, et al., Phys. Rev. B **73**, 144428-1-7 (2006).

Development of Nuclear Resonant Inelastic X-ray Scattering at High Pressure and Low Temperature

Wenli Bi,[1] Jiyong Zhao,[1] Jung-fu Lin,[2] Stanislav Sinogeikin,[3] Michael Y. Hu,[1] E. Ercan Alp[1]
[1]Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439, USA
[2]Geology Sciences, The University of Texas at Austin, Austin, TX, 78712, USA
[3]High Pressure Collaborative Access Team, Geophysical Laboratory, Carnegie Institution of Washington, Argonne, IL 60439, USA

Nuclear resonant inelastic x-ray scattering (NRIXS) has been applied to variety of systems under pressure. However, such studies at low temperature and high pressure have eluded researchers thus far due to technical challenges. At beamline 3ID of the APS, we have developed a miniature panoramic DAC and a He flow cryostat to enable the new experimental capability of NRIXS at high pressure and low temperature. The prototype of the setup has been described in Ref [1]. Most recently we have incorporated a gas membrane system for in-situ pressure change and designed a new cryostat, which allows liquid He flowing further down to the DAC holder to achieve lower tempearure. The lowest temperature of 9 K was achieved on the DAC with this setup. The new instrumentation is conducive to carry out simultaneous NRIXS, Mössbauer spectroscopy measurements, in-situ online x-ray diffraction experiment, and in-situ pressure readout using ruby fluorescence. The new capability has been applied to study the evolution of lattice dynamics and magnetism at high pressure and low temperature from both ^{151}Eu and ^{57}Fe isotopes in single crystalline sample Eu^{57}Fe$_2$As$_2$. The instrumentation will be described in detail and experiment results will be discussed.

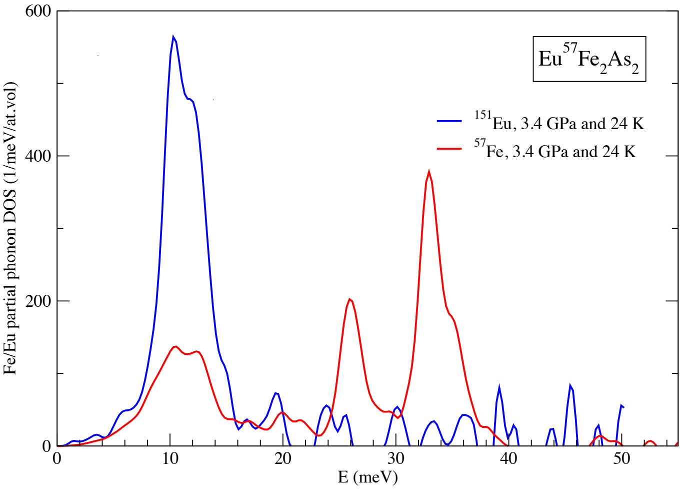


Figure 2: Partial phonon density of states of ^{57}Fe and ^{151}Eu in single crystalline sample Eu^{57}Fe$_2$As$_2$ at 3.4 GPa and 24 K. The measurements were done with x-ray beam along c-axis of the sample.

References

[1] W. Bi, J. Zhao, J. Lin, Q. Jia, M.Y. Hu, C. Jin, R. Ferry, W. Yang, V. Struzhkin, and E.E. Alp, J. Synchrotron Rad. **22**, 760-76 (2015).

This work is supported by U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences under contract DE-AC02-06CH11357, and the Consortium for Materials Properties Research in Earth Sciences (COMPRES) [National Science Foundation (NSF) EAR 06-49658].

Resonance scattering in determining of the gas molecular state

A. V.P. Filippov, Yu. A. Lauer

National Research Nuclear University MEPhI (Moscow Engineering Physics Institute),

Determination of the gas molecular state is an important task in the chemical industry and in the manufacture of semiconductor devices, where toxic gases such as phosphine (PH_4) can be produced. Activation analyses allows determining only the elemental composition but not the gas molecules formula. Resonance methods were used for the determination of the gas molecular state [1, 2]. These methods based on the resonance absorption of gamma radiation by iron atoms located in the compounds, for example, in the form of ferric chloride and on the recording of the transmitted radiation. To determine of the gas state the blotting paper is sated with iron chloride solution. Then a test gas passes through the paper. This gas reacts with ferric chloride and changes the chemical state of the iron atoms. The changes in the chemical state of the iron atoms in ferric chloride in comparison with its initial state allows to judge about the state of the gas passed through the paper. This method has several disadvantages. It requires a large amount of gas, and also leads only to slight changes in the spectra of resonant absorption as the ferric chloride is a paramagnetic compound and the compounds formed by reacting with the investigated gas can be as paramagnetic compounds too. This complicates the interpretation of the spectra.

It is possible to use scattering radiation such as conversion electrons. The high sensitivity to changing of the iron chemical state gives the possibility for chemical analyzing of the gas interacting with surface with iron atoms. In this paper the investigations of some gases chemical states are described. In order to obtain the direct prove , as an example, two gases (NH_3 and N_2H_4) with the same chemical elements but with different chemical formulae were investigated. It was made the interaction of these gases with thin films of ^{57}Fe. These films of ^{57}Fe were obtained on the specimens from aluminum, glasses and beryllium. The films thicknesses were changed from 100 to 500 A° It was found that more useful and informative thicknesses are 400-500 A°. The determination of the gases chemical states were made by comprising Mossbauer spectra obtained using CEMS of the initial films and after interaction with gases. The differences of the isomer shifts and quadrupole splitting were found to exist for these two gases. For gas NH_3 isomer shift $IS= 0.325\pm0.025$ mm/s, quadrupole splitting $QS=0.969 \pm0.025$ mm/s , for gas N_2H_4 $IS= 0.472\pm0.030$ mm/s, $QS= 0.924\pm0.030$ mm/s In order to determine the chemical state of complex gases with the poor interaction with iron the special method and chamber were developed. The idea of this method is to obtain and accelerate the ions of investigating gases in electrical field. The using this method and chamber gives the possibility to obtain an interaction of complex compounds with thin films of ^{57}Fe. The obtained results prove the real possibility of resonant scattering to determine the chemical state of gases.

References

[1] I.P. Suzdalev. Dinamicheskie effecti v gamma-resonansnoy spectroscopii. Atomisdat, 1979. (Rus).

[2] L.P. Baranova et all. Journal of ecology and industrial safety. **1**, 35 (2008). (Rus).

Element-Resolved Thermodynamics of Magnetocaloric $LaFe_{13\text{-}x}Si_x$

M. E. Gruner[1,2,3] , W. Keune[1], B. Roldan Cuenya[4], C. Weis[1], J. Landers[1], S. I. Makarov[1], D. Klar[1], M. Y. Hu[5], E. E. Alp[5], J. Zhao[5], M. Krautz[3], O. Gutfleisch[6], and H. Wende[1]

[1]Faculty of Physics and Center for Nanointegration Duisburg-Essen, University of Duisburg-Essen, 47048 Duisburg, Germany

[2]Forschungs-Neutronenquelle Heinz Maier-Leibnitz, FRM-II, TU Munich, 85748 Garching, Germany

[3]IFW Dresden P.O.Box 270116, 01171 Dresden, Germany

[4]Department of Physics, Ruhr-University Bochum, 44780 Bochum, Germany

[5]Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA

[6]Materials Science, TU Darmstadt, 64287 Darmstadt, Germany

Among the outstanding magnetocaloric materials are $LaFe_{13\text{-}x}Si_x$ – based systems ($1.0 \leq x \leq 1.6$) [1,2]. A first-order magnetic transformation occurs at T_C, combined with an abrupt isostructural volume decrease of 1% upon loss of magnetic order. The isothermal entropy change ΔS_{iso} across T_C is usually divided up as $\Delta S_{iso} = \Delta S_{mag} + \Delta S_{lat} + \Delta S_{el}$, i.e., contributions from the magnetic, lattice (vibrational) and electronic degrees of freedom, respectively, although mixed interactions may enhance ΔS_{iso} significantly [3]. - By combination of ^{57}Fe nuclear resonant inelastic X-ray scattering (NRIXS) in zero external magnetic field and first-principles calculation in the framework of density functional theory, we demonstrate significant changes in the element-resolved vibrational density of states (VDOS) across T_C (Fig. 1) from the ferromagnetic (FM) to the paramagnetic (PM) phase of the magnetocaloric $LaFe_{13\text{-}x}Si_x$ [4]. In particular, we observe the abrupt disappearance of a distinct phonon peak when entering the PM state. These changes originate from the itinerant electron metamagnetism associated with Fe and lead to a pronounced magneto-elastic softening despite the large volume decrease at T_C upon heating. The observed increase in lattice entropy (ΔS_{lat}) associated with the Fe subsystem is significant and contributes cooperatively with ΔS_{mag} and ΔS_{el}. Recent detailed NRIXS studies across T_C in a 0.9-T external magnetic field confirm the significant contribution of ΔS_{lat}.

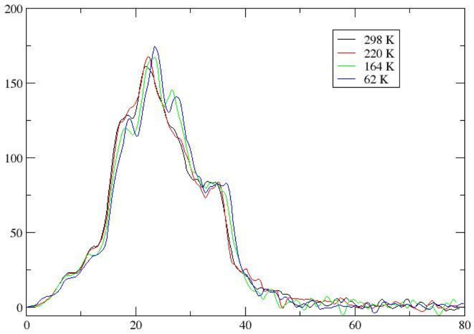


Figure 1: Fe-projected VDOS of $LaFe_{11.6}Si_{1.4}$ at T = 62, 164, 220 and 299 K. (T_C = 189 K).

References

[1] S. Fujieda, A. Fujita and K. Fukamichi, APL **81**, 1276 (2002).
[2] J. Liu, M. Krautz, K. Skokov, T. G. Woodcock and O. Gutfleisch, Acta Mater. **59**, 3602 (2011).
[3] T. Mukherjee, S. Michalski, R. Skomski, D. J. Sellmyer and C. Binek, PRB **83**, 214413 (2011).
[4] M. E. Gruner, W. Keune, B. Roldan Cuenya, C. Weis, J. Landers, S. I. Makarov, D. Klar, M. Y. Hu, E. E. Alp, J. Zhao, M. Krautz, O. Gutfleisch and H. Wende, PRL **114**, 057202 (2015).

Element-Resolved Thermodynamics of Magnetocaloric LaFe$_{13-x}$Si$_x$

M. E. Gruner[1,2,3] , W. Keune[1], B. Roldan Cuenya[4], C. Weis[1], J. Landers[1], S. I. Makarov[1], D. Klar[1], S. Salamon[1], M. Y. Hu[5], E. E. Alp[5], J. Zhao[5], M. Krautz[3], O. Gutfleisch[6], and H. Wende[1]

[1]Faculty of Physics and Center for Nanointegration Duisburg-Essen, University of Duisburg-Essen, 47048 Duisburg, Germany

[2]Forschungs-Neutronenquelle Heinz Maier-Leibnitz, FRM-II, TU Munich, 85748 Garching, Germany

[3]IFW Dresden P.O.Box 270116, 01171 Dresden, Germany

[4]Department of Physics, Ruhr-University Bochum, 44780 Bochum, Germany

[5]Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA

[6]Materials Science, TU Darmstadt, 64287 Darmstadt, Germany

Among the outstanding magnetocaloric materials are LaFe$_{13-x}$Si$_x$ – based systems ($1.0 \leq x \leq 1.6$) [1,2]. A first-order magnetic transformation occurs at T_C, combined with an abrupt isostructural volume decrease of 1% upon loss of magnetic order. The isothermal entropy change ΔS_{iso} across T_C is usually divided up as $\Delta S_{iso} = \Delta S_{mag} + \Delta S_{lat} + \Delta S_{el}$, i.e., contributions from the magnetic, lattice (vibrational) and electronic degrees of freedom, respectively, although mixed interactions may enhance ΔS_{iso} significantly [3]. - By combination of ^{57}Fe nuclear resonant inelastic X-ray scattering (NRIXS) in zero external magnetic field and first-principles calculation in the framework of density functional theory, we demonstrate significant changes in the element-resolved vibrational density of states (VDOS) across T_C (Fig. 1) from the ferromagnetic (FM) to the paramagnetic (PM) phase of the magnetocaloric LaFe$_{13-x}$Si$_x$ [4]. In particular, we observe the abrupt disappearance of a distinct phonon peak when entering the PM state. These changes originate from the itinerant electron metamagnetism associated with Fe and lead to a pronounced magneto-elastic softening despite the large volume decrease at T_C upon heating. The observed increase in lattice entropy (ΔS_{lat}) associated with the Fe subsystem is significant and contributes cooperatively with ΔS_{mag} and ΔS_{el}. Recent detailed NRIXS studies across T_C in a 0.9-T external magnetic field confirm the significant contribution of ΔS_{lat}.

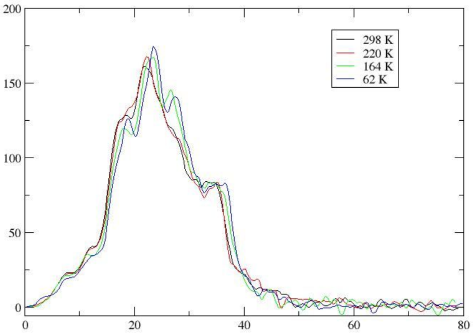


Figure 1: Fe-projected VDOS of LaFe$_{11.6}$Si$_{1.4}$ at T = 62, 164, 220 and 299 K. (T_C = 189 K).

References

[1] S. Fujieda, A. Fujita and K. Fukamichi, APL **81**, 1276 (2002).
[2] J. Liu, M. Krautz, K. Skokov, T. G. Woodcock and O. Gutfleisch, Acta Mater. **59**, 3602 (2011).
[3] T. Mukherjee, S. Michalski, R. Skomski, D. J. Sellmyer and C. Binek, PRB **83**, 214413 (2011).
[4] M. E. Gruner, W. Keune, B. Roldan Cuenya, C. Weis, J. Landers, S. I. Makarov, D. Klar, M. Y. Hu, E. E. Alp, J. Zhao, M. Krautz, O. Gutfleisch and H. Wende, PRL **114**, 057202 (2015).

Update of the nuclear resonant scattering studies at extreme environmental conditions at 3ID, APS

J.Y. Zhao, W. Bi, D.Z. Zhang, M. Hu, J.F. Lin[1], S. Sinogeikin[2], T. Toellner and E. E. Alp

Advanced Photon Source, Argonne National Laboratory, 9700 S Cass Ave, Argonne, IL 60439, USA
[1]Department of Geology Sciences, The University of Texas at Austin, Austin, TX 78712, USA
[2]HPCAT, Geophysical Laboratory, Carnegie Institute of Washington, Argonne, IL 60439, USA

Nuclear resonant scattering (NRS) at 3ID, APS, has been intensively used for high pressure research using diamond anvil cell (DAC) techniques in last decade for applications of geophysics and materials science to study material properties such as thermal dynamics, hyperfine interactions, sound velocities and magnetic behaviours. A unique laser heated diamond anvil cell (LHDAC) system has been implemented as a dedicated system for the NRS study at 3ID. The pressure of ~ Mbar and temperature of ~ 3000K have been achieved. A recent upgrades of the LHDAC system and some recent research results will be presented in this talk.

In order to study the magnetic and superconducting properties of the newly discovered iron pnictides under high pressure and low temperature using the NRS, we have developed a cryogenic high-pressure system suitable for both nuclear resonant inelastic x-ray scattering (NRIXS) and nuclear forward scattering studies. By using a newly developed mini-DAC, the distance between the sample placed inside the cryostat and the APD detector placed outside of the vacuum jacket is minimized to about 12 mm. By directly flowing liquid helium through the mini-DAC holder, the temperature on the sample as low as 9 K has been achieved. A gas-driven membrane cell mechanics is used to precisely adjust the pressure of the mini-DAC at low temperature while an on-line Ruby pressure measurement system is in place. In this presentation, technical details of the system will be described, and some preliminary experimental results on EuFe2As2 superconducting materials will be discussed.

References

[1] W.Bi, J.Y. Zhao, J.F. Lin, Q. Jia, M. Y. Hu, C. Jin, R. Ferry, W. Yang, V. Struzhkin and E. E. Alp, J. of Synchrotron Radiation, 22 (2015).

This work is supported by U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences under contract DE-AC02-06CH11357. The project is partially supported by the Consortium for Materials Properties Research in Earth Sciences (COMPRES)

Nuclear Inelastic Scattering and Geophysics: Triumphs and Setbacks

C. McCammon[1], *C. Prescher*[1,a], *R. Sinmyo*[1], *K. Glazyrin*[1,b], *I. Kupenko*[1,2], *A. Kantor*[1,2],
V. Potapkin[1,2], *V. Cerantola*[1,2], *A.I. Chumakov*[2], *R. Rüffer*[2], *L. Dubrovinsky*[1]

[1]*Bayerisches Geoinstitut, Universität Bayreuth, Bayreuth, Germany*
[2]*ESRF, Grenoble, France*
[a]*now at: University of Chicago, Argonne, USA;* [b]*now at: DESY, Hamburg, Germany*

Comparison of laboratory measurements of elastic wave velocities of mantle minerals with seismic data constitutes one of the foundations upon which knowledge of the Earth's interior is based. *In situ* measurements are important, because some transitions (for example, spin transitions) are not quenchable, and may influence the elastic properties of iron-containing minerals. In the laboratory setting, techniques such as ultrasonics, Brillouin scattering, and impulsive stimulated scattering offer attractive possibilities to measure sound velocities directly [1], but stumble when faced with the challenge of iron-containing phases at pressures and temperatures of the deep Earth's interior. Technical developments in the past decade involving third generation synchrotron sources as well as methods for laser heating in the diamond anvil cell have opened new possibilities for such measurements, notably nuclear inelastic scattering (NIS) where sound velocities of iron-containing minerals can be determined through direct measurement of the partial density of states.

NIS has notched up a number of success stories in geophysics in the recent past, a number of which have involved our group. The technique is well suited to measurements of phases where iron is the dominant cation, for example studies of iron carbide [Fe_7C_3] that reveal a softening of shear wave velocity above 50 GPa, providing an explanation for the anomalous elastic properties of the Earth's inner core [2]. For solid solutions the local nature of the NIS method can lead to complications; however corrections have been developed to compensate for the effects of next-nearest neighbour configurations in ferropericlase [(Mg,Fe)O] to produce sound velocities that agree well with the results of other methods [3]. Finally there are some cases for which NIS has so far failed to yield useful data, notably the Earth's most abundant mineral, bridgmanite [$(Mg,Fe)(Si,Al)O_3$ perovskite], that constitutes more than 50% of the Earth by volume.

The presentation will examine critical aspects of NIS methodology within the context of sound velocity determination of iron-containing phases relevant to the Earth's interior, particularly at high pressure and high temperature conditions, showcasing both its triumphs and setbacks, and will include a perspective for the future.

References

[1] J. D. Bass, S. V. Sinogeikin, B. Li, Elements **4**, 165 (2008).
[2] C. Prescher, L. Dubrovinsky, E. Bykova, I. Kupenko, K. Glazyrin, A. Kantor, C. McCammon, M. Mookherjee, Y. Nakajima, N. Miyajima, R. Sinmyo, V. Cerantola, N. Dubrovinskaia, V. Prakapenka, R. Rüffer, A. Chumakov, M. Hanfland, Nature Geoscience **8**, 220 (2015).
[3] R. Sinmyo, K. Glazyrin, C. McCammon, I. Kupenko, A. Kantor, V. Potapkin, A. I. Chumakov, R. Rüffer, L. Dubrovinsky, Physics of the Earth and Planetary Interiors **229**, 16 (2014).

Structural Transformations in Metallic Glasses followed by *in situ* Nuclear Forward Scattering of Synchrotron Radiation

M. Miglierini[1,2], V. Procházka[3], and R. Rüffer[4]

[1]*Institute of Nuclear and Physical Engineering, Slovak University of Technology, 812 19 Bratislava, Slovakia*
[2]*Regional Centre of Advanced Technologies and Materials, Palacky University, 771 46 Olomouc, Czech Republic*
[3]*Faculty of Science, Palacky University, 771 46 Olomouc, Czech Republic*
[4]*ESRF-The European Synchrotron, CS40220, 38043 Grenoble Cedex 9, France*

Structural transformations that are taking place in Fe-based metallic glasses are of paramount importance and they are studied with variety of methods. Here, we report on the use of *in situ* nuclear forward scattering (NFS) of synchrotron radiation. NFS provides simultaneous information on changes in both structural arrangement and hyperfine interactions in real time. In this respect, it is superior to other *in situ* techniques. Two types of experiments were performed: (i) isothermal heat treatment of the investigated metallic glasses, and (ii) their exposure to dynamically changing temperature with a heating rate of 10 K/min. Some *in situ* heat treatments were eventually performed in a weak external magnetic field of 0.652 T.

The following compositions of metallic glasses were studied: $Fe_{90}Zr_7B_3$, [1, 2] (see Fig. 1), $Fe_{81}Mo_8Cu_1B_{10}$ [3], and $(Fe_{1-x}Co_x)_{76}Mo_8Cu_1B_{15}$ [4]. They ensure formation of the so-called nanocrystalline alloys in which crystalline grains with the size of several nanometres are formed in the early stage of structural transformation. Due to high sensitivity of the NFS technique, it was possible to clarify the contribution of structurally different regions in the investigated samples, viz. amorphous residual matrix, newly formed nanocrystalline grains, and the so-called interfacial regions that are ascribed to Fe atoms located at the surfaces of the nanograins.

This work was supported by the grant LO1305.

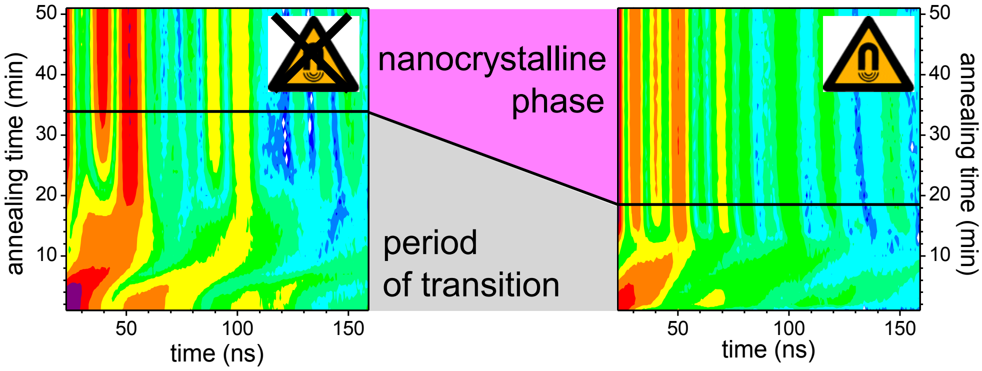


Figure 1: Contour plots of NFS taken from isothermally annealed (@ 753 K) $Fe_{90}Zr_7B_3$ metallic glass without (left) and with (right) external magnetic field (0.652 T).

References

[1] M. Miglierini, V. Prochazka, S. Stankov, P. Svec Sr., M. Zajac, J. Kohout, A. Lancok, D. Janickovic, and P. Svec, Phys. Rev. B **86**, 020202(R) (2012).

[2] M. Miglierini, V. Procházka, R. Rüffer, and R. Zbořil, Acta Mater **91**, 50 (2015).

[3] V. Procházka, V. Vrba, D. Smrčka, R. Rüffer, P. Matúš, M. Mašláň, and M. Miglierini, J. Alloy. Compounds **638**, 398 (2015).

[4] M. Miglierini, M. Pavlovič, V. Procházka, T. Hatala, G. Schumacher, and R. Rüffer, Physical Chemistry Chemical Physics, (2015) DOI: 10.1039/C5CP00245A.

Creation and application of sapphire nanostructured substrates

Muslimov A.E., Butashin A.V. and Kanevsky V.M.

A.V. Shubnikov Institute of Crystallography Russian Academy of Sciences,
Leninskii prospekt 59, Moscow, 119333 Russia

Different microelectronic devices, optics for visible light and X-rays usually require the super-polished substrates of different crystalline materials. In the present report we show the possibilities to use the nanostructured sapphire substrates for this purpose. It is demonstrated that the terrace-step structure of such substrates gives the possibility to obtain single-crystal thin layers of CdTe, ZnO on top of them. More that such structure of substrates allows creating of oriented gold nanowires on the whole surface of substrates. These nanowires can be used in photonics and as contacts for elements of microchips. The terrace-step nanostructure was forming on atomically smooth vicinal surfaces of sapphire crystals, which were subjected to mechanical, chemical and thermal treatment. The steps from monoatomic (0.22 nm) to 3 nm and more can be formed on the sapphire surface by changing of vicinal angle and the modes of heat treatment. It is shown that the regularity of the terrace-step nanostructure is deteriorating with increasing of steps height. Also, the studies of terrace-step nanostructure evolution was carried out, and it shows the possibility of increasing the steps height by the thermal annealing. The experiment results are interpreted in terms of minimizing the surface energy and surface diffusion processes.

The use of sapphire substrates with regular nanorelief allowed us to choose the conditions of CdTe films epitaxy by MBE method to ensure their higher structural perfection. The film growth rate was 100-150 nm per hour. The direct application by thermal evaporation was carried out to increase the rate of growth of the CdTe film to 1 micron per hour. In this case the inclined geometry of the evaporation experiment was used and the substrate was situated at angle of 450 degrees to the flow. A positive result was achieved with the use of substrates with high-steps terrace nanostructure with the order of 2-3 nm. Also, the method of suppressing the domain structure in the ZnO films epitaxy on the substrates with regular nanorelief was offered. During the research of gold deposition on nanostructured sapphire substrates by the developed technique the conditions of golden nanodots and nanowires formation were found. It was revealed by AFM that the location of golden nanoparticles is regular and repeats the surface profile. Further optical experiments have revealed the peculiarity in the s-polarized optical wave reflectivity. This effect appears when the polarization vector coincides with the surface structure direction and is determined by resonance between s-polarized wave and surface plasmons. First results obtained in fabrication of regular golden nanoparticles on sapphire substrates which can be applied as functional devices in nonlinear optics.

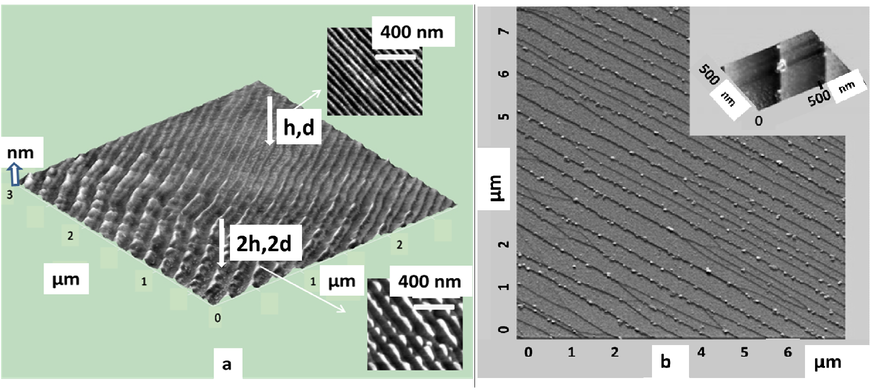


Figure 1: Studies of terrace-step nanostructure evolution (a); ordered gold nanostructures (b).

Lattice Dynamics of Wire-Like Eu Nano-Structures

O. Waller[1,2], P. Piekarz[3], S. Ibrahimkutty[2,4], D. G. Merkel[5], A. Seiler[1,2], R. Rüffer[5], A. I. Chumakov[5],
T. Baumbach[1,2,4], K. Parlinski[3], and S. Stankov[1,2]

[1]Laboratory for Applications of Synchrotron Radiation, Karlsruhe Institute of Technology, Germany
[2]Institute for Photon Science and Synchrotron Radiation, Karlsruhe Institute of Technology, Germany
[3]Institute of Nuclear Physics, Polish Academy of Sciences, Poland
[4]Synchrotron Radiation Source ANKA, Karlsruhe Institute of Technology, Germany
[5]European Synchrotron Radiation Facility, France

The fundamental understanding of the atomic vibrations in low-dimensional systems is essential for the elucidation and control of phenomena such as superconductivity, propagation of sound and heat, thermal stability and thermoelectricity that often strikingly deviate from those of bulk materials [1]. The comprehensive knowledge of the vibrational dynamics requires a complete determination of the phonon dispersion relations and/or phonon density of states (DOS) that define thermal and elastic properties of materials [2].

Applying *in situ* nuclear inelastic scattering [3] on ^{151}Eu and first-principles calculations we studied the lattice dynamics of nanowire-like high aspect ratio Eu structures. These nano-structures are formed upon deposition of monolayer (ML) coverages of Eu on stepped (110)Nb buffer layers epitaxially grown on the A-plane Al_2O_3. The experimental results reveal the presence of a remarkable vibrational anisotropy for a nominal Eu coverage of 2ML. Additionally, a systematic shift of the phonon DOS to high energies leads to a significant suppression of low-energy phonon modes and an enhancement of the high-energy states with respect to that of *bcc* Eu. An increase of the Eu coverage results in a shift of the phonon DOS to lower energies, that is accompanied by a gradual reduction and finally disappearance of the vibrational anisotropy. The observed effects are explained by the evolution of the surface morphology from a wire-like towards an island-like surface.

S.S. acknowledge the financial support by the Initiative and Networking funds of the President of the Helmholtz Association and the Karlsruhe Institute of Technology (KIT) for the Helmholtz-University Young Investigators Group "Interplay between structure and dynamics in epitaxial rare-earth nanostructures" contract VH-NG-625.

References

[1] M. A. Stroscio and M. Dutta “Phonons in Nanostructures”, Cambridge University Press (2005).
[2] B. Fultz, Progress in Material Science **55**, 247 (2010).
[3] S. Stankov, T. Ślęzak, M. Zając, M. Ślęzak, M. Sladecek, R. Röhlsberger, B. Sepiol, G. Vogl, N. Spiridis, J. Łażewski, K. Parliński, and J. Korecki in “Mössbauer Spectroscopy: Applications in Chemistry, Biology, Industry, and Nanotechnology” Editors: V. K. Sharma, G. Klingelhoefer and T. Nishida, Wiley, (2013).

Lattice Dynamics of Ultrathin Metal-Oxide Interfaces

O. Waller[1,2], P. Piekarz[3], S. Ibrahimkutty[1,2], D. G. Merkel[4], A. Seiler[1,2], R. Rüffer[4], A.I. Chumakov[4], T. Baumbach[1,2,5], K. Parlinski[3], and S. Stankov[1,2]

[1]Laboratory for Applications of Synchrotron Radiation, Karlsruhe Institute of Technology, Germany
[2]Institute for Photon Science and Synchrotron Radiation, Karlsruhe Institute of Technology, Germany
[3]Institute of Nuclear Physics, Polish Academy of Sciences, Poland
[4]European Synchrotron Radiation Facility, France
[5]Synchrotron Radiation Source ANKA, Karlsruhe Institute of Technology, Germany

Nanoscale metal-oxide interfaces find important applications in the today's nanotechnology. Prominent examples are heterogeneous nanocatalysts [1] and gate layers in the CMOS-based micro- and nanoelectronics [2]. These applications entirely rely on the formation of ultrathin metal-oxide interfaces with tailored properties. Due to the finite thickness of these layered structures, often down to a single atomic layer of material, the atomic vibrations are expected to significantly deviate from those of the bulk counterparts. This affects their thermodynamic, elastic and, via the electron-phonon interactions, their electronic properties. Therefore, the comprehensive understanding of the lattice dynamics of nanoscale metal-oxide interfaces is of fundamental importance for the future nanotechnological developments.

Employing *in situ* nuclear inelastic scattering [3] on ^{151}Eu and first principles calculations we have investigated the lattice dynamics of fcc Eu nanoislands stabilized on a sub-nanometer thick EuO interface layer naturally formed on the Nb(110) surface [4]. Unexpectedly, the analysis revealed that the EuO interface exhibits thermoelastic properties that are close to that of the bulk material.

S.S. acknowledges the financial support by the Initiative and Networking funds of the President of the Helmholtz Association and the Karlsruhe Institute of Technology (KIT) for the Helmholtz-University Young Investigators Group "Interplay between structure and dynamics in epitaxial rare-earth nanostructures" contract VH-NG-625. The European Synchrotron Radiation Facility (ESRF), Grenoble is acknowledged for the synchrotron beamtime at the Nuclear Resonance beamline ID18.

References

[1] Y. Yamada, C.-K. Tsung, W. Huang, Z. Huo, S.E. Habas, T. Soejima, C.E Aliaga, G.A. Somorjai, and P. Yang, Nature Chem. **3**, 372 (2011).
[2] S.D. Ha and S. Ramanathan, J. Appl. Phys. **110**, 071101 (2011).
[3] S. Stankov, T. Ślęzak, M. Zając, M. Ślęzak, M. Sladecek, R. Röhlsberger, B. Sepiol, G. Vogl, N. Spiridis, J. Łażewski, K. Parliński, and J. Korecki in "Mössbauer Spectroscopy: Applications in Chemistry, Biology, Industry, and Nanotechnology" Editors: V. K. Sharma, G. Klingelhoefer and T. Nishida, Wiley, (2013).
[4] O. Bauder, A. Seiler, S. Ibrahimkutty, D. G. Merkel, B. Krause, R. Rüffer, T. Baumbach, and S. Stankov J. Cryst. Growth **400**, 15 (2014).

Correlation Investigation on the Water and Iron Specific Vibration States in Prussian Blue Analogues by Nuclear Resonant Scattering Technique

X. Li[1,2], A. I. Rykov[1], W. Xu[3], D. Chen[3], J. Zhao[4], M. Y. Hu[4], W. Bi[4,5], T. S. Toellner[4], E. E. Alp[4], and J. Wang[1]

[1]Mössbauer Effect Data Center & Laboratory of Catalysis and New Materials for Aerospace, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China (Email: wangjh@dicp.ac.cn)
[2]University of Chinese Academy of Sciences, Beijing 100049, China
[3]Institute of High Energy Physics, Chinese Academy of Sciences, Beijing,100049, China (xuw@mail.ihep.ac.cn)
[4]Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439, USA
[5]COMPRES, University of Illinois at Urbana Champaign, Urbana, Illinois, 61801

Prussian blue analogues (PBAs), as one kind of metal–organic porous materials, exhibit various functional properties, such as electrochemical activity, hydrogen storage, reactive adsorption removal of radioactive ^{137}Cs and catalytic properties. The existence of interstitial and coordinated water molecules in the structure of PBAs is of great importance for their reactive adsorption and catalytic properties. The water molecules should also have great affect on the vibration states of Fe. However, the details of the correlation among water and iron specific vibration states within PBAs have remained unknown. Therefore, the structural and dynamical information of Fe regarding the water molecules in PBAs is of great interests from both fundamental and technological perspectives.

The nuclear resonant scattering (NRS) spectroscopy is powerful tool to study the hyperfine interactions, magnetic properties and site-specific vibrational dynamics. In this contribution, we will firstly report the structural and dynamical information of H_2O-Fe in the structure of Fe-Co PBA. The content of water could be flexibly modulated by heating at low temperatures, such as 60 ^{o}C in air or argon atmosphere (Figure. 1, left). The conventional Mössbauer spectra (CMS) as well as the synchrotron Mössbauer spectra (SMS) are shown in Figure 1, center, which reveal the change of relative ratio of Fe^{II}/Fe^{III} before and after 60 ^{o}C heat treatment in air. Then we will focus on the correlation investigation on the water and iron-specific vibration states through the nuclear resonance inelastic X-ray scattering spectroscopy (NRIXS, Figure 1, right).

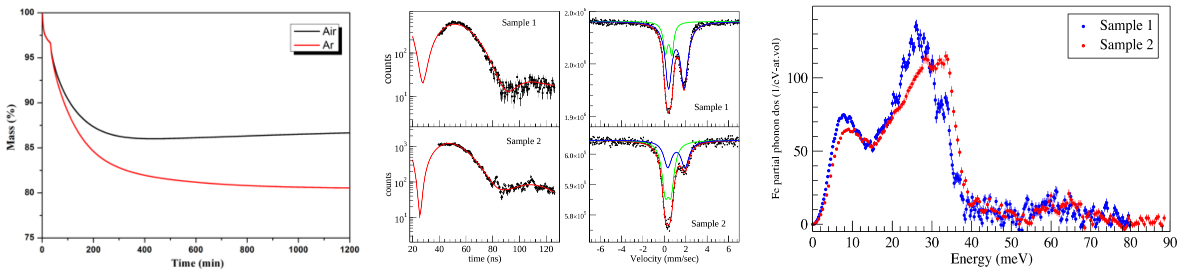


Figure 1: TG-DSC of Fe-Co PBA heating at 60 ^{o}C in air and argon atmosphere (left), the NRIXS of before and after heat treatment (right), and SMS and CMS data on the same samples (center).

The High Energy Photon Source (HEPS) in China is planned and holds great promises among the low emittance and high energy storage rings. Given the large number of potential users in Mössbauer spectroscopy, physics, materials sciences, and chemistry, the NRS program should be one of the unique techniques to be realized at this new photon source. We are developing the necessary optics and detector technology to build a dedicated beamline at HEPS. As part of this effort, we have recently tested the performance of a meV-monochromator of NRS in the framework of bilateral collaborations between the Institute of High Energy Physics and Advanced Photon Source. The monochromator with as-designed energy resolution allows us to perform NRS experiment on the aforementioned catalysts, opening an avenue for catalyst investigations.

Lattice dynamics in FeSe-based superconductors with T_C up to 42 K derived from Fe phonon-DOS.

G. Wortmann[1], V. Ksenofontov[2], S.I. Shylin[2], and S.A. Medvedev[3]

[1]*Department of Physics, University of Paderborn, 33095 Paderborn, Germany*
[2]*Institute of Inorganic and Analytical Chemistry, Johannes Gutenberg University Mainz, 55099 Mainz, Germany*
[3]*Max-Planck Institute for Chemical Physics of Solids, 01187 Dresden, Germany*

Within the novel superconducting (s.c.) Fe-based systems, FeSe with its most simple PbO-type structure and its derivatives (abbreviated as the "11" family) could be clue compounds for the understanding of the s.c. mechanisms in these systems. In particular, the dramatic increase of T_C under pressure from 8.5 K at ambient pressure to 36.7 K at 9 GPa observed by us [1] points to a new s.c. mechanism in these systems which is still under debate. Within the 11-family, T_C can be also increased by the substitution of Se by Te, resulting in T_C ~14 K for $FeSe_{0.5}Te_{0.5}$. Another way to increase T_C is the intercalation of other species between the FeSe layers, e.g. Na^+. Rb^+, Cs^+ ions with T_C = 32 K for $Rb_{0.6}Fe_{1.8}Se_2$ [2]. Recently, intercalation of Li/NH_3 and related species has proven to increase to T_C above 40 K [3]. In all these FeSe-based systems the s.c. mechanism is still an open question.

Here we present a systematic study of the lattice dynamics and thermodynamic properties in various FeSe-based superconductors with T_C up to 42 K, as derived from the local Fe phonon density-of-states (DOS) measured by ^{57}Fe nuclear inelastic scattering (NIS) of synchrotron radiation and compare the derived results with those obtained from conventional ^{57}Fe-Mössbauer spectroscopy. In our previous ^{57}Fe-NIS study of the Fe phonon-DOS in s.c. FeSe as function of temperature and pressure [4] we could prove that electron-phonon interactions could not be the main mechanism for superconductivity in these systems. These ^{57}Fe-NIS phonon studies were continued on other FeSe-based s.c. systems, $FeSe_{0.5}Te_{0.5}$ with T_C = 14 K and $Rb_{0.8}Fe_{1.6}Se_2$ with T_C = 32 K, using the single-crystalline samples to exemplify significant differences in the phonon-DOS and derived elastic properties when measured parallel or perpendicular to the crystalline c-axis. Finally, we present very recent studies of the Fe phonon-DOS in Li/NH_3 intercalated FeSe with T_C = 42 K. This system is most important for a principal understanding of the s.c. mechanism, because the structure of s.c. FeSe-layers is contained with only minute changes, where on the other hand the electronic properties, here the conduction band structure, are strongly modified by Li/NH_3 intercalation as proven by our ^{57}Fe-Mössbauer study [5].

For all above systems we derive local Debye temperatures and recoilless fractions (Mössbauer-Lamb factors) from the measured phonon-DOS g(E) as well as from the so-called reduced DOS, $g(E)/E^2$, in the low energy region, as done in our previous study of $Fe_{1.01}Se$ [4] similar to the case of a ^{119}Sn-NIS study of SnO with the same PbO-type structure as FeSe [6]. We will discuss why the derived Debye temperatures may be different when derived by the two above modes, also when derived from the second-order Doppler shift (SOD) measured with Mössbauer spectroscopy, as discussed in our recent study of Li/NH_3-FeSe [5]. We also derive and compare the energy position of the well-resolved acoustic and optical phonon modes as function of temperature, especially above and below T_C. Together with conventional ^{57}Fe-Mössbauer spectroscopy, we can exclude any lattice softening connected with T_C as claimed previously for some of the above systems, e.g. $FeSe_{0.5}Te_{0.5}$ [7].

References

[1] S. Medvedev et al., Nature Mater. **8**, 630 (2009).
[2] V. Ksenofontov et al., Phys. Rev. B **84**, 180508 (2011).
[3] M. Burrard-Lucas et al., Nature Mater. **12**, 15 (2013).
[4] V**.** Ksenofontov et al., Phys. Rev. B **81**, 184510 (2010).
[5] S.I. Shylin et al., Europhys. Lett. **109**, 67004 (2015).
[6] H. Giefers et al., Phys. Rev. B **74**, 094303 (2006).
[7] J. Linden et al., Solid State Commun. **151**, 130 (2011).