MATERIALS SCIENCE BY NUCLEAR METHODS

NUCLEAR METHODS IN MATERIALS SCIENCE: WHY DO WE NEED THEM?

Particles as local probes and tools of manipulation of condensed matter

Condensed matter is all around us. Solids and liquids form our planet, our buildings, food, drinks, artworks, drugs, but also the living creatures, plants, animals and even ourselves. Improving properties and understanding the structure and governing phenomena of hard and soft condensed matter to our benefit is an issue of ultimate importance. Conventional investigation and engineering methods are *macroscopic*, a serious limitation in many cases. Photons, neutrons, accelerated ions, positrons, i.e. particles from radioactive sources or from accelerator beams act as *local probes* to investigate condensed matter and they are also used to *modify material properties on an atomic scale*. Consequently, nuclear methods play an indispensable role in materials science (MS) and technology alike.

Here the term 'materials science' is used in a broader sense than usual. By this phrase we mean all disciplines related to the analysis and study of physical-chemical phenomena and deliberate modification of the properties of hard or soft condensed matter.

Applying nuclear methods in MS implies a specified knowledge and research infrastructure. These are put together at the Department of Materials Science by Nuclear Methods (MS Department) of the Wigner Research Centre for Physics, Hungarian Academy of Sciences (MTA Wigner FK). The department's mission is to conduct experimental basic research in this field and to develop nuclear solid-state methods and their theories as well as the related infrastructures in home laboratories and at large international research facilities.

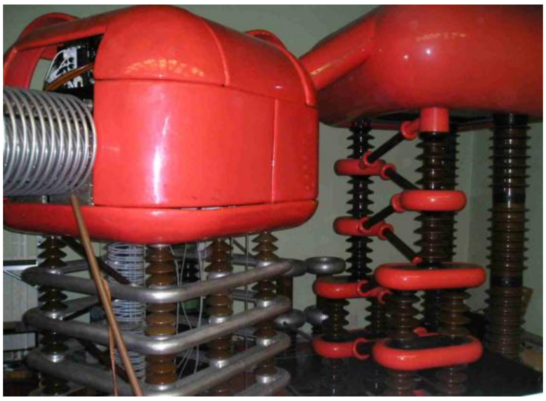
The MS Department of the MTA Wigner FK consists of the co-workers of two research units of the former RMKI, viz. the Department of Nuclear Physics and the Nuclear Analysis Group of the Department of Biophysics.

Due to the complexity of the methods and infrastructures involved, the activity of the MS Department is methodologically defined, the applications ranging from spintronics to preserving cultural heritage and from chemistry and life sciences to studying new functional materials. Past experience proved that methodological coherence and thematic diversity is a real strength of research of the department. Below some activities in the last two years are listed.

Operating, developing and using research infrastructures

The department operates and develops major pieces of research infrastructure of the MTA Wigner FK.

- The EG-2R electrostatic accelerator and the NIK heavy-ion implanter coupled by a common implantation/scattering chamber is a unique accelerator complex. It enables *in situ* ion-beam analysis of ion-implanted samples as well as the proton microbeam and external millibeam PIXE studies on the EG-2R.



The NIK heavy-ion implanter of 450 kV terminal voltage

- The molecular-beam epitaxy (MBE) facility, (at the time of the report, Hungary's only machine

The MECA-2000 molecular-beam epitaxy facility for preparing metallic thin-film samples under ultrahigh-vacuum conditions of the kind) is used to prepare metallic thin films. About 50–100 samples are prepared in each year for research groups in Hungary for our collaborators in Germany and Russia.

- The GINA polarised neutron reflectometer accomplished at the Budapest Neutron Center (BNC) is open to transnational access in the FP7 Integrated Activity (IA) NMI3 of the EC.

The GINA polarised neutron reflectometer in operation at the neutron guide hall of the Budapest Neutron Center (BNC)

- The magnetic thin-film laboratory comprises Mössbauer spectrometers, radiochemistry facilities and direct access to the MBE machine.
- The X-ray spectrometry laboratory, with the external millibeam PIXE facility of EG-2R and the fixed and mobile XRF spectrometers, are open to transnational access in frames of the FP7 IA CHARISMA of the EC.
- In the HELIOS laser laboratory of the MTA Wigner FK SZFKI, a pump-probe setup is being realised on the basis of a (1kHz-35fs-4mJ) Coherent Legend Elite laser amplifier. This installation will allow us to perform femtosecond-resolved transient optical absorption spectroscopy, which shall be a synergetic completion of our ultrafast laser and theory programmes.
- An X-ray laboratory to develop optics has been realised recently; this laboratory also hosts the computing workstation that we use to model the electronic structure of molecular systems.

The accelerator complex and the MBE are parts of the Hungarian Ion-beam Physics Platform (HIPP), a consortium with the Institute for Nuclear Research, Hungarian Academy of Sciences (ATOMKI, Debrecen). In 1997, three academic research institutes formed a consortium under the name of Budapest Neutron Centre (BNC), presently also including the MTA Wigner FK. The magnetic thin-film laboratory is part of the national Network of Mössbauer Laboratories (NML). HIPP, BNC and NML are recognised as *Strategic Research Infrastructures* of NEKIFUT, the National Research Infrastructure Survey and Roadmap Programme.

NMI3:	http://neutron.neutron-eu.net/n_nmi3
HIPP:	http://hipp.atomki.hu/
BNC:	http://www.bnc.hu/
CHARISMA:	http://www.charismaproject.eu/
NEKIFUT:	http://www.nekifut.hu

On beam-time application and cooperation grounds alike, MS Department researchers are regular users of synchrotrons and hard X-ray free electron lasers— European Synchrotron Radiation Facility (ESRF), Grenoble, France, Advanced Photon Source, Argonne, UAS, Swiss Light Source (SLS), Villigen, Switzerland, Linear Coherent Light Source, Stanford, USA, SACLA, Japan and research reactors — FRM-II, TU München Germany, IBR-2, JINR, Dubna, Russia.

FUNCTIONAL NANOSTRUCTURES

Interaction of superconducting and ferromagnetic layers in proximity

Using polarised neutron reflectometry combined with the resonance enhancement of the neutron intensity in a waveguide layer structure the inverse proximity effect of the superconducting (SC) transition upon the magnetic structure of the ferromagnetic (FM) layer in Fe/V FM/SC bilayers were observed in a joint project with MPI Solid State Research, Stuttgart. An antiparallel alignment of the induced magnetisation in the SC close to the FM layer was found for a d_{Fe} = 1 nm and theory predicts a sign depending on the FM layer thickness. Varying the layer thickness and the ferromagnetic element the origin of the induced magnetic layer within the S layer is revealed.

Participation in development of magnetic films for neutron optics

Using polarised neutron reflectometry (PNR) on GINA, magneto-optical Kerr effect, X-ray and other techniques, researchers of the department significantly contributed to the development efforts of Mirrotron Ltd. towards its mass production of doped Si/Fe supermirrors for various neutron optics applications.

Reciprocity in a scattering experiment

Reciprocity requires the scattering amplitude be symmetric upon transposition of detector and source. Reciprocity violation in magneto-optical gyrotropy, a well-known property of the Mössbauer nuclear medium was studied. Following the theoretical elucidation by L. Deák and T. Fülöp we experimentally found large non-reciprocity in nuclear resonance scattering at special orientations of the magnetic hyperfine fields (L. Deák et al, *PRL (2012)*). Recently, in a successful experiment at the Petra III synchrotron, Hamburg we found a non-reciprocity in the phase of the scattering amplitude using stroboscopic detection of the nuclear resonance scattering of synchrotron radiation.

ION–SOLID INTERACTIONS

In-situ spectroscopic ellipsometry

In-situ spectroscopic ellipsometry measurements during ion implantation give new insights into the depth-dependent evolution of the disorders and morphology changes. These kinds of investigation are based on the fact that the ion-implantation-induced disorder changes the complex dielectric function of the implanted material. In cooperation with MFA, a commercial M-88 type spectroscopic ellipsometer with rotating analyzer produced by J.A. Woollam Co. Inc. was mounted on the vacuum chamber of the heavy-ion implanter at an incident angle of 75°. The method was demonstrated on single-crystal germanium implanted by 200-keV Sb ions at RT. The time evolution of the ellipsometric Ψ parameter, i.e., Ψ as a function of ion dose has been determined by in-situ spectroscopic ellipsometry at three different wavelength values (382 nm, 418.4 nm and 450 nm). The change of the refractive index can be interpreted as amorphisation and void formation caused by ion implantation.

RBS on 3D-structured objects

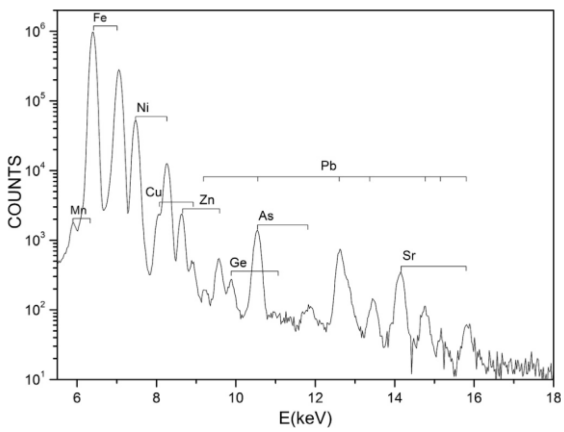
For the interpretation of Rutherford backscattering spectrometry (RBS) spectra taken on 3D-structured samples (porous materials, non-continuous layers, etc.) a Monte-Carlo simulation program, RBS-MAST has been developed. This code is an essential tool in studying ion-solid interactions on the nanoscale by conventional RBS.

In cooperation with MFA, the capability of this method was demonstrated on nanosphere lithography (NSL) masks. A self-organised layer of colloidal spheres was used as a mask for a lithographic step such as illumination, ion implantation, deposition or etching. Due to ion-nanoparticle interactions, the ion implantation through this mask not only leads to the patterning of the substrate but also to the deformation of the nanomask itself. Geometrical transformation of the nanoscaled silica spheres into ellipsoids was observed after Xe ion irradiation. The geometry of the nanoparticles and the composition of the system were successfully determined by conventional RBS using the RBS-MAST code.

MFA: Research Centre for Natural Sciences, Institute for Technical Physics and Materials Science, http://www.mfa.kfki.hu

Non-destructive analysis of art and archaeological objects by energy-dispersive x-ray spectrometry

The MS Department is an important part of the Hungarian BNC platform of the Fixlab of the CHARISMA EU FP7 project offering the possibility for external-millibeam PIXE and XRF analysis of art and archaeological objects in addition to the reactor-based neutron methods. A recent exciting result of the combined use of these techniques was the proof of the meteorite origin of small beads from two burials in Gerzeh, Northern Egypt. These beads are the earliest known iron artefacts dated to circa 3200 BC. The key argument of the proof was the detection of Ge by external-beam PIXE. Two of the three fully corroded beads investigated showed spots with germanium of estimated concentrations of about 30 µg/g, and reaching up to about 100 µg/g in individual spots.



PIXE spectrum of an iron bead clearly showing the presence germanium (Ge)

X-RAY SPECTROSCOPY WITH SYNCHROTRON RADIATION

Femtosecond-resolved X-ray spectroscopy

After having established time-resolved X-ray Emission Spectroscopy (XES) and Resonant Inelastic X-ray Scattering with picosecond time resolution in recent years, we have installed a crystal spectrometer and performed the first femtosecond-resolved XES at both existing hard X-ray free electron laser, the LCLS in Stanford, US, and SACLA in Japan. The studied systems included switchable and light-harvesting molecular systems, the results revealed interesting electron, molecular, and solvent dynamics on the few and sub picosecond time scales.

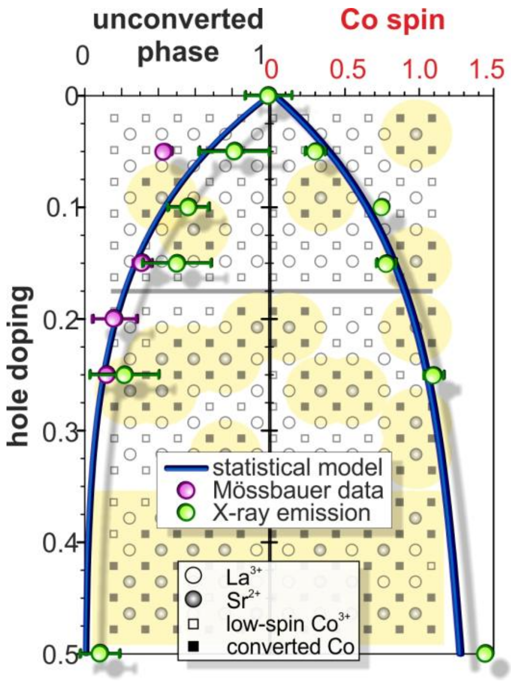
Microscopic origin of the nanoscale magnetic-electronic phase separation in LSCO

Investigating the roots of a nanoscale magneto-electronic phase separation (responsible for their magnetoresistance as well as cooperative electric and magnetic phase transitions) in bulk Sr-doped $LaCoO_3$ (LSCO), we have combined local spectroscopic techniques as synchrotron XES and laboratory Mössbauer spectroscopy to identify and characterise the clusterisation process. A simple model based on the random distribution of the doping Sr ions describes well both the doping-driven evolution of the separated phases and the variation of the Co spin state.

THEORY, DATA EVALUATION

Mössbauer spectroscopy, nuclear resonant scattering of SR

An efficient DWBA computer code for diffuse Mössbauer reflectometry was developed and applied for determining the domain correlation function of antiferromagnetic multilayers. Furthermore, the theory of polarisation-dependent conversion-electron Mössbauer spectra for arbitrary angle of incidence has been established making available the determination of the layer magnetisations by Mössbauer polarimetry with an uncertainty as low as a few degrees. Both theories were integrated in the general simultaneous fitting computer code FitSuite.



Effect of Sr^{2+} (hole) doping on the fraction of the insulating phase as well as the spin momentum of the Co in $La_{1-x}Sr_xCoO_3$.

Ab initio modelling of molecular systems

Molecules with spin-state transitions have high potential as switchable molecular devices. However, to design and improve such systems we need a deep understanding of the electronic structure, including all electronic states that are related to the switching phenomena. We found that for such systems the ground and excited state electronic structure can be described with Time-Dependent Density Functional Theory (TD-DFT) almost as good as with the much more costly multireference second-order perturbation theory method, CASPT2.

Mössbauer spectroscopy is a widely-used local probe but the interpretation of the spectra often requires help from theory. We have studied a chemically diverse and extended set of 66 iron compounds with Density Functional Theory and provided clear recipes for obtaining reliable isomer shift and quadrupole splitting values.

Ion-beam analysis

RBX, DEPTH and RBS-MAST codes for simulation of IBA spectra are being developed continuously.

FitSuite:	**http://www.fs.kfki.hu/**
RBX, DEPTH, RBS-MAST:	**http://mffo.rmki.kfki.hu/ion**