Dr Alexei Kuzmin, Head of the Laboratory of Materials and Structure Investigations, discusses the role of X-ray absorption spectroscopy in materials science and the latest developments in this field at the Institute of Solid State Physics of the University of Latvia (ISSP UL)

Solving the structure of materials: in search of the grail

Establishing the structure of a material is one of the most important goals of any research in materials science and nanoscience. It is crucial knowledge for understanding and optimising material properties and ultimately influencing their practical applications. The structure is also the starting point for theoretical studies, based on numerical simulations and aimed at exploration and the prediction of new materials.

X-ray absorption spectroscopy (XAS) is an excellent probe of the local atomic structure in crystalline, nanocrystalline, and disordered solids, liquids and gases. Moreover, in multicomponent materials, XAS allows the independent studying of the local environment around atoms of different types. The method is applicable at both high and low concentrations of the chemical element of interest and can be implemented in a wide range of *in-situ* and *in-operando* conditions.

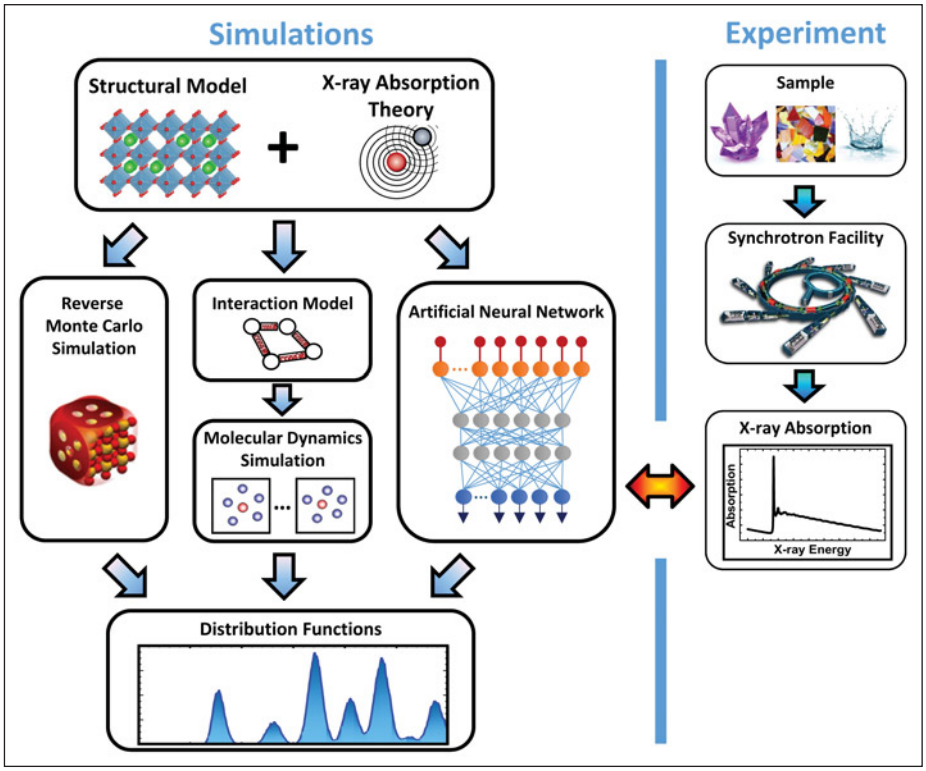

Fig.1 Scheme of X-ray absorption spectra analysis using reverse Monte Carlo, molecular dynamics and artificial neural network methods

The role of synchrotrons

The success of XAS is based solely on the use of large-scale synchrotron radiation facilities. 16 synchrotron sources are currently available in EU Member States, and there are over 50 sources worldwide. There are also a number of the laboratory XAS spectrometers, but they cannot currently compete with synchrotrons. The advantages of synchrotrons as an X-ray source are their wide and continuous spectral range, high flux, and brilliance. Synchrotron radiation also has other useful properties as a characteristic polarisation and pulsed temporal structure.

The availability of synchrotron radiation facilities provides scientists from the university laboratories with access to an innovative infrastructure that allows for competitive research at the forefront of modern science. Such transnational organizations are often the birthplace of new ideas and the emergence of cooperation. They also play important roles in disseminating obtained results and serve as educational centres for new users and, especially, young researchers.

ISSP UL

ISSP UL, being the leading research centre in the field of material science in Latvia, has a long tradition in using European synchrotron centres. A significant part of its activities is traditionally dedicated to XAS. Pioneering XAS experiments have been conducted in the 1980s and early 1990s at the Frascati ADONE synchrotron radiation source (which closed in 1993) and later at the Orsay LURE storage rings, which stopped in 2006. During that time, prominent results were achieved in the field of electrochromic metal oxide materials for smart coatings, as well as in studies of superconducting materials and contrast agents for medical diagnostics. This was a starting point for the formation of a team in ISSP UL specialising in synchrotron-based experiments and XAS. This is now a well-known speciality of the Institute.

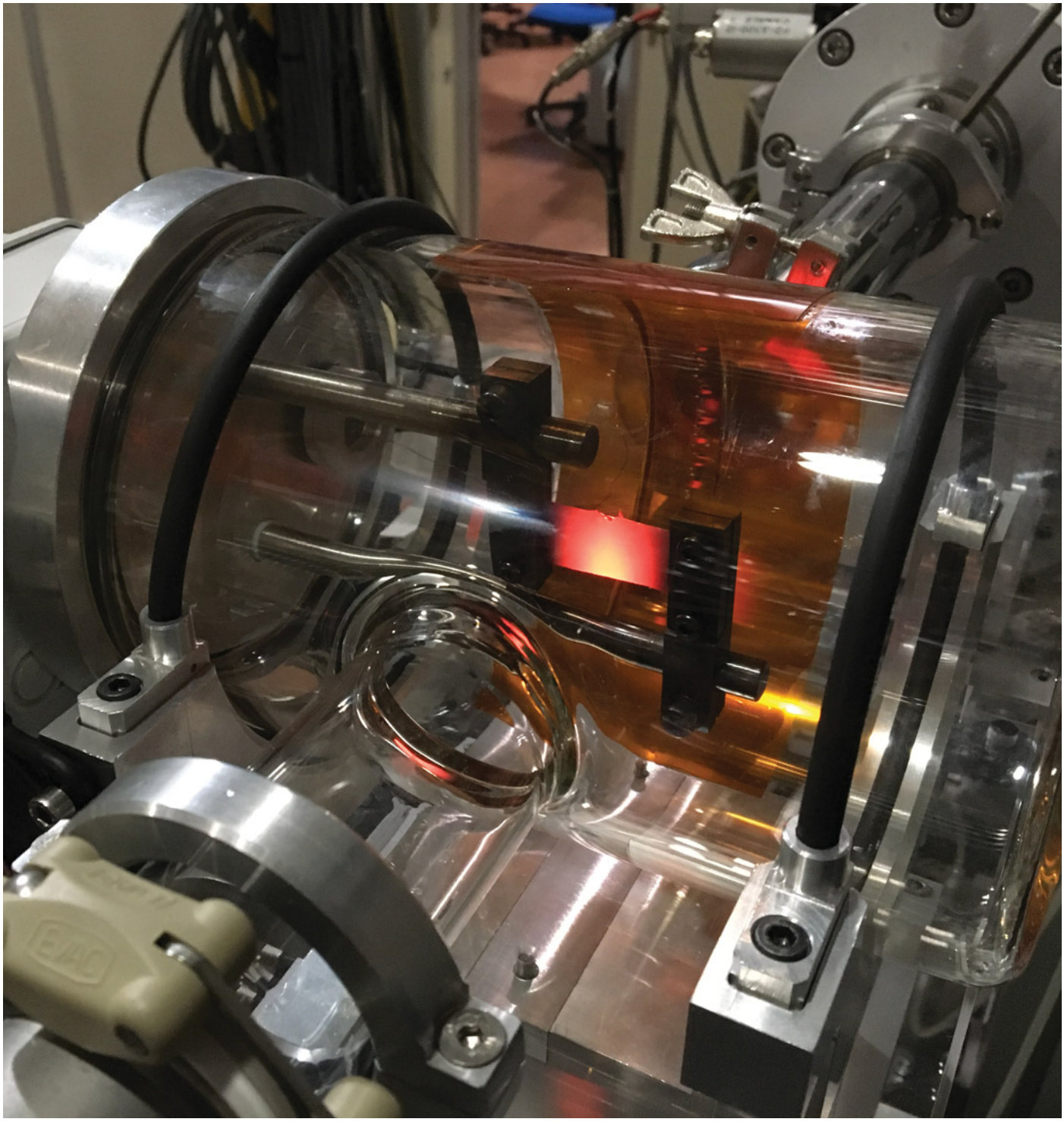

Fig. 2 Experimental set-up of the high-temperature *in-situ* X-ray absorption spectroscopy measurements of Fe foil

In the early 2000s, a collaboration between the ISSP UL team and partners from France, Italy, and Estonia within the European Commission's Sixth Framework Programme project 'X-TIP' led to the development and demonstration of a new tool for nanoscience which combines XAS with scanning near-field optical microscopy (SNOM). The XAS-SNOM microscope placed at a synchrotron beamline collects the X-ray excited optical luminescence (XEOL) signal in the near field through a tapered optical fibre probe. The latter is attached to an oscillating quartz tuning fork and is used to record simultaneously with XEOL the topographical image of the sample surface. As a result, element-specific contrast becomes attainable in SNOM, and information on the local structure and electronic properties of materials can be obtained with a spatial resolution down to the nanometre scale.

An alternative approach, based on the sample mapping using the focused X-ray beam to probe non-homogeneity of material, has been employed by the ISSP team within the MNT-ERA.NET project, which has been realised in collaboration with Forschungszentrum Jülich in 2009-2012. It has been demonstrated that XAS at the Fe K-edge is sensitive enough to evidence oxygen vacancy clustering around iron ions during resistive switching in Fe-doped $SrTiO_3$ thin film memristive devices.

Recent advances in analysis

Simultaneous with experimental activities at large-scale facilities, ISSP UL has been amongst the pioneers in the development of advanced data analysis methods. The development over the past 10 years is focussed to increase the reliability and amount of structural information that one can extract from X-ray absorption spectra (see Fig. 1).

The currently-available approaches developed by ISSP UL rely on atomistic simulations such as

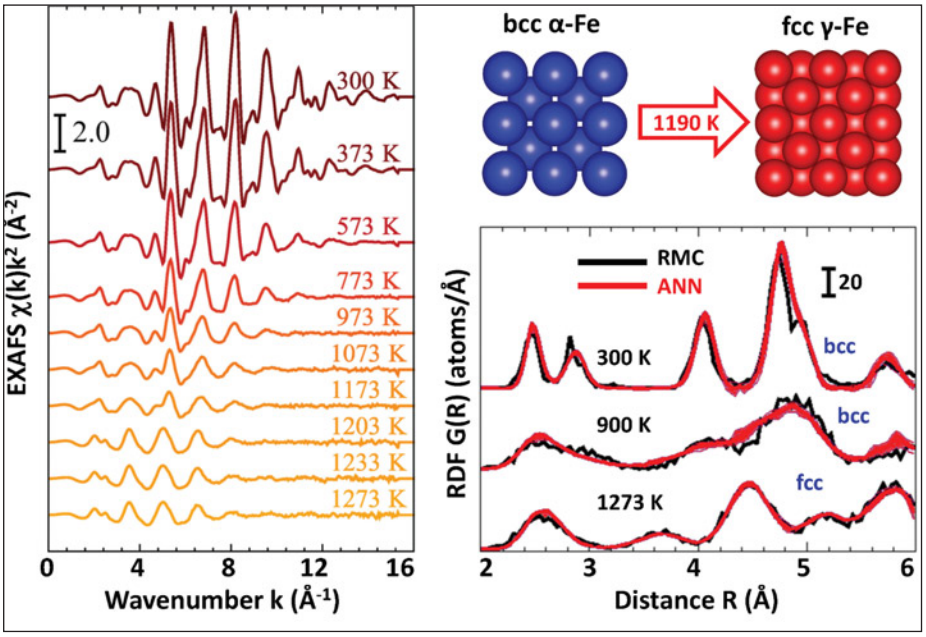

Fig. 3 Left panel: Experimental Fe K-edge extended X-ray absorption fine structure (EXAFS) of iron foil for temperatures between 300 and 1273 K. Right panel: Comparison of the radial distribution functions (RDFs) G(R) for iron in body-centred cubic (bcc)and face-centred cubic (fcc) phases obtained by reverse Monte Carlo (RMC) and artificial neural network (ANN) methods. For details see: J. Timoshenko *et al.*, Phys. Rev. Lett. 120 (2018) 225502, doi: 10.1103/PhysRevLett.120.225502.

molecular dynamics (MD) and reverse Monte-Carlo (RMC) methods, which are employed together with *ab initio* theory of X-ray absorption. However, these simulations are often extremely computationally demanding. Therefore, their practical applications are based on the intensive use of high-performance computing. The advantage of these methods is that they provide a natural way to incorporate static and thermal disorder into the structural model. Unlike conventional analysis, which deals with a set of structural parameters, both methods give the results in terms of atomic configurations, which include information on atom-atom and bond-angle distributions and correlations.

In spite of the fact that the extraction of structural information is the main goal of XAS studies, the agreement between the experimental and calculated X-ray absorption spectra in combination with methodology developed in ISSP UL can also be used to validate the interatomic potentials employed in MD simulations of materials. Such an approach is of interest because XAS experiments can be relatively easily performed at the required temperature and pressure. In this case, XAS acts as a bridge between experiment and theory. Currently, this approach is being employed by ISSP UL researchers to study, for example, oxide-dispersion-strengthened alloys for the future fusion and advanced fission reactors within the framework of the EURATOM/EUROfusion projects.

The power of the XAS method is often negated due to the need for a time-consuming analysis of experimental data. This issue becomes critical when it is necessary to take a quick decision during the experiment to guide some process or reaction. In this case, one can rely on the use of machine learning algorithms. In particular, the artificial neural network (ANN), pre-trained in advance using thousands of theoretical models generated by MD simulations, can be used for rapid X-ray absorption spectra analysis. Such an approach has been recently utilised to follow structural changes in iron during a high-temperature phase transition from ferritic to austenitic phase. The work performed by ISSP UL in collaboration with the researchers from Stony Brook University and Brookhaven National Laboratory has attracted remarkable attention of the scientific community. The advantage of this approach is that pre-trained ANNs can be easily shared, which allows other researchers to analyse their data without having to perform the tedious ANN training process on their own.

A look into the future

There are many other applications of XAS, which are stimulated by materials demand and developments in instrumentation. For example, experiments at extreme conditions and time-dependent studies of ultrafast electronic and structural dynamics continuously attract considerable interest from researchers. The accessible timescales range from minutes to tens of picoseconds at synchrotron sources and go down to femtoseconds at X-ray free-electron laser (X-FEL) facilities. As a result, quantitative structural and kinetic data can be obtained on catalytic and photo-induced processes, chemical reactions, and phase transitions in the solid and liquid states. These groundbreaking research activities will undoubtedly stimulate and promote further developments in the XAS field.

About the Institute and CAMART²

The Institute of Solid State Physics of the University of Latvia is an internationally-recognised leader with 40 years of experience in the material sciences and cross-disciplinary topics in Latvia, which provides competitive research and innovative solutions for industrial applications. The Institute offers modern infrastructure for different kind of material synthesis and analysis that also serve the research needs of scientific and industrial partners. Most of the advanced tools are installed in the clean room facilities.

A H2020 Teaming project, CAMART² is one of the largest projects in Latvian science to date, and received European Commission funding for strategic development, as well as assistance from the top players in the field from Sweden – Royal Institute of Technologies (KTH) and Research Institutes of Sweden (RISE).

The project's objective is to strengthen the Institute's position as a significant regional science, innovation, and technology transfer centre, as well as within the Latvian state, within Europe, and, indeed, internationally. This objective is already being achieved, with the Institute now world-renowned for the development of knowledge and skills in synchrotron-based experiments and XAS.

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