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L19

POWDER DIFFRACTION AND SOLID ELECTROLYTES, CASE OF METAL HYDRIDOBORATES

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Interest in metal hydrides was initially driven by the potential to develop efficient and safe on-board hydrogen stores working close to ambient pressure and temperature. In search for hydrides with higher gravimetric storage capacity, the researchers concentrated on hydrides based on light atoms, among others on Li and Na salts containing hydridoborate anions such as borohydride BH_4^- or *closo*-hydridoborate $\text{B}_{12}\text{H}_{12}^{2-}$ [1]. The hydrogen absorption-desorption cycling in complex hydrides still needs more chemical ideas due to relatively strong covalent bonding. Unexpectedly, the high mobility of alkali metal cations in some complex hydrides has opened the door for their application as battery materials, mainly as *solid-state electrolytes* (SSE).

Replacing the liquid electrolyte by SSE offers several advantages: *i*) a solid material is more thermally stable, thus enhancing the overall safety of the battery; *ii*) being less prone to the dendrite penetration, it enables the use of alkali metals as negative electrodes and *iii*) acting as physical layer between the two electrodes, it has a beneficial effect on the cell performance [2].

Among the different classes of SSE, the metal hydridoborates have received particular interest, being soft, highly stable toward oxidation and exhibiting fast ion conductivity, enabled by an entropically-driven phase transition. Such transitions generally occur above room temperature (*rt*), and it is therefore necessary to frustrate the anionic lattice, for example by anion mixing or mechanical energy (Figure 1) to bring the superionic regime down to *rt* [3-8].

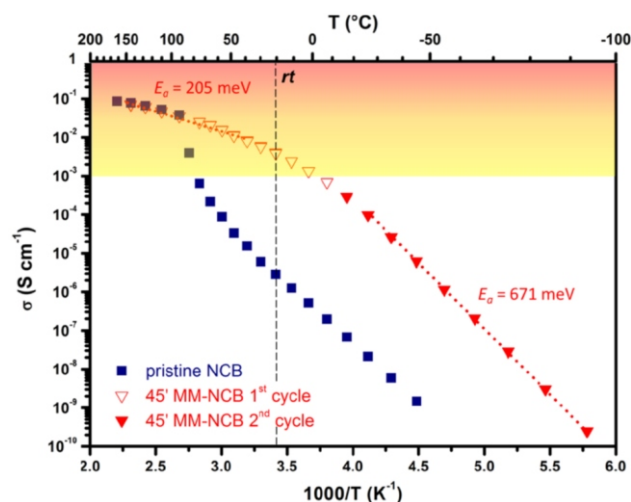


Figure 1. DC Conductivity evolution as function of the temperature for pristine (blue squares) and ball-milled- $\text{NaCB}_{11}\text{H}_{12}$ (red triangles). For the sake of clarity, the superionic regime ($> 1 \text{ mS cm}^{-1}$) has been highlighted in the graph.

The hydrogen storage and mobility of the cations in light complex hydrides depends on the structural features, pathways available in the anion packing and on the anion thermal motion. While the latter requires important experimental and theoretical effort, the first two parameters can be easily quantified from crystal structures obtained by

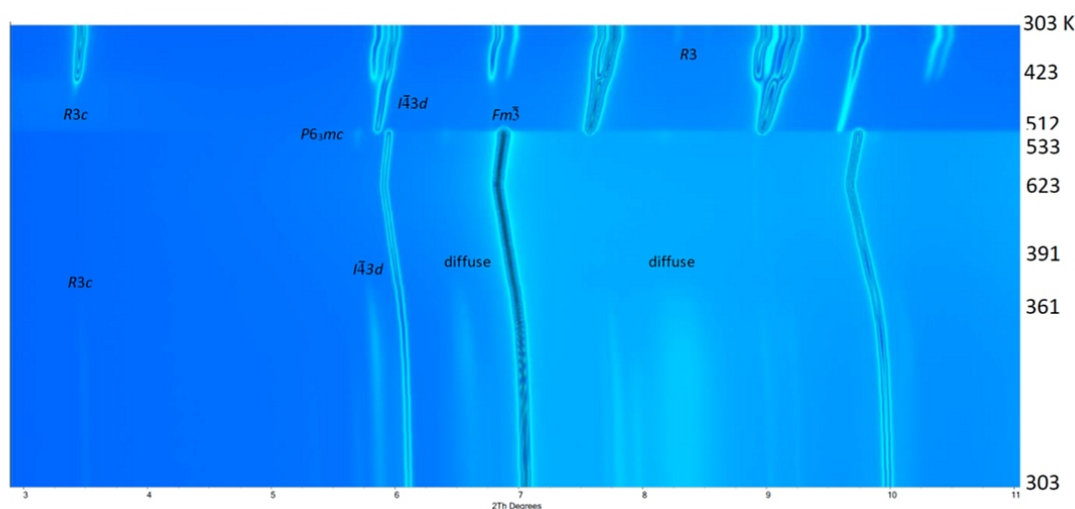


Figure 2. Temperature dependent synchrotron radiation XPD data measured on dry $\text{CsCB}_{11}\text{H}_{12}$ sample with fast heating/cooling rate of 10 K/min , wavelength $= 0.64113 \text{ \AA}$. The peaks of different polymorphs are labelled with their space group symbols. Observed diffuse intensity is labelled too.



X-ray powder diffraction (XPD). Main difficulties of crystal structure determination by XPD with hydridoborate samples are low crystallinity, overcome by global optimization (direct space) methods [9], and a multiphase character of the samples, solved by “decomposition aided indexing” [10] as was the case of $\text{CsCB}_{11}\text{H}_{12}$ [11] shown in Figure 2. The case of molecular compound $\text{C}_2\text{B}_{10}\text{H}_{12}$ demonstrates the effect of inter-cluster interaction on stabilization of various crystal structure symmetries [12].

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L20

NEUTRON PHYSICS LABORATORY ŘEŽ AND ITS INSTRUMENTATION FOR INVESTIGATION OF MATERIALS STRUCTURE AND MICROSTRUCTURE

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Neutron Physics Laboratory (NPL) of CANAM infrastructure (operated by Nuclear Physics Institute Řež), canam.ujf.cas.cz/npl, and its instrumentation for investigation of structure and microstructure of advanced materials will be presented. NPL consist of five neutron diffractometers (residual stress scanning, powder diffraction, small-angle neutron scattering, in-situ thermomechanical

tests and neutron-optics testing diffractometers) and of three nuclear analytical techniques (Neutron Depth Profiling, Prompt Gamma Activation Analysis, Neutron Activation Analysis). The layout is depicted in Fig. 1. The laboratory provides open access to academic users on the basis of proposals continuously evaluated by the international Scientific Selection Panel. In December 2022, NPL

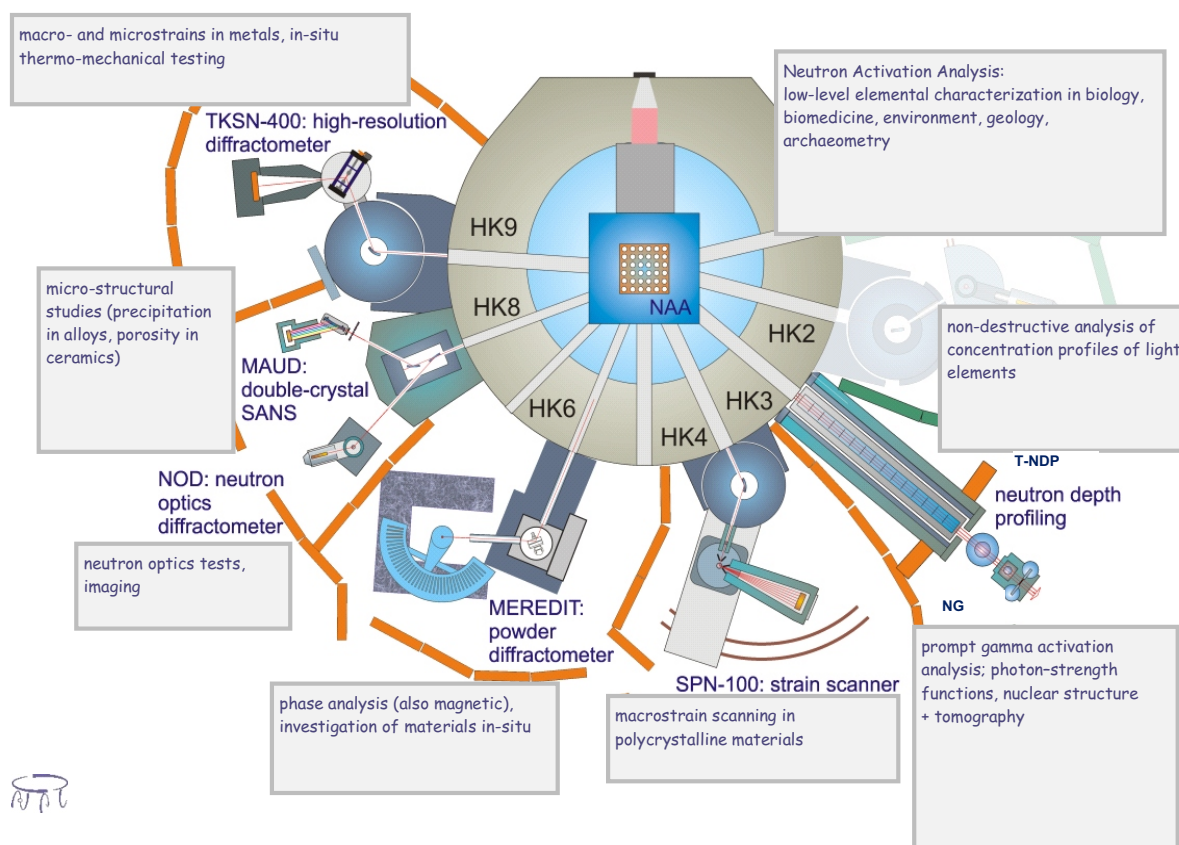


Figure 1. Layout of NPL facilities in the LVR-15 research reactor (operated by Research Centre Řež) hall.

became the tenth member of the League of Advanced Neutron Sources (LENS). The LENS comprises European-level research facilities that support the international scientific community by providing access to instruments for, and/or expertise in, neutron science.

Recently, several instruments were upgraded by new neutron-optics components, by new sample environment, as well as by sample preparation and auxiliary facilities. The strain scanner was equipped by radial neutron collimator, SANS diffractometer by a new bending holder with long analyzer crystal. New portable neutron camera facilitates sample adjustment within sample environment. A system for concurrent in situ neutron diffraction, me-

chanical testing and acoustic emission detection was obtained. Nuclear analytical techniques were improved by supermirror neutron guide, by electrochemical impedance analyzer, by cryogenic mill and by electrical fusion furnace.

Selected examples from the studies with help of neutron physics facilities carried out at NPL will be presented: on Li depth distribution in thin Li-ion batteries, on the application of Neutron Activation Analysis, on deformation mechanisms in magnesium alloy, on mesoporous silica morphology, on complex metal oxides structure, and on residual stress in steel component fabricated by Selective Laser Melting.

L21

XRD LABORATORY AND MATERIALS INVESTIGATION AT RESEARCH CENTRE ŘEŽ

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At Research Centre Řež (Centrum výzkumu Řež s.r.o., CVŘ) in the department of Material Analysis (before Material and Mechanical Properties), where analysis of materials was commonly performed by microscopy techniques, was added a powder X-ray diffraction (XRD) facility for analysis preferentially of irradiated materials, as a complement to the existent analytical techniques. Annexed to the XRD facility is the preparation room of irradiated geological samples, building materials and ceramics located in the hot-cells facility building [1].

The milling and preparation of specimen for XRD analysis of irradiated, or radioactive, materials is carried out inside of a shielded glove box, which is kept at negative pressure to avoid leakage of radioactive powder outside the glove box, afterwards the samples are transferred to the XRD laboratory in a sealed container to be analysed in a diffractometer Empyrean (Malvern-PANalytical) with a Co-anode X-ray tube, with the option of automatic loading of samples, and remote operation [2].

Currently at CVŘ XRD lab several research topics connected to nuclear energy are being investigated, they can be divided in two groups:

1) Influence of the neutron irradiation on concrete aggregates [3] used as biological shield in nuclear reactors. Concrete aggregates (e.g. quartz, feldspars) under irradiation experience a radiation-induced volumetric expansion, which can cause cracking of the concrete thus reducing its lifetime. Using XRD we can monitor the changes in lattice

parameters and unit cell volume of the mineral aggregates after irradiation at different neutron fluences.

2) Monitoring of stability of materials used as fixation matrices for radioactive waste in a simulated environment of a deep geological repository. The materials used as fixation matrices vary from cement, clays [4], geopolymer, mixture of clay and cement. Those matrices are storage under synthetic water, simulating the underground water that could fill the geological repository, afterwards changes in the mineral composition are monitored on the surface and inside the matrices using XRD.

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L22

MP_TOOLS: FROM MOLECULAR DYNAMICS SIMULATIONS TO DIFFUSE SCATTERING MAPS

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To extract information on disordered structures from scattering data one often has to compare model-based intensities with the observed ones. The progress in computing techniques in last decades permits to produce realistic models of crystalline lattices by a variety of approaches ranging from *ab initio* DFT methods via molecular dynamics (MD) to phase-field models based on the Landau formalism.

With this progress in place the bottleneck has shifted from producing supercell models to generating the corresponding diffuse scattering distributions in reciprocal space.

The principal issue was due to the fact that scattering amplitudes from a distorted lattice could not be summed up using fast Fourier transform algorithms (FFT) because of the displacement phase factor $\exp(-i\mathbf{Q}\mathbf{R})$ being \mathbf{Q} -dependent.

As a consequence, many efforts in recent years have been restricted to simple models on small supercells [1,2] or to more involved pair distribution function (PDF) analysis [3-5], where the summation problem is reduced to a single dimension. Nevertheless, the efficiency of PDF model generation in direct space for large supercells and large correlation distances needed for good quality Fourier transforms was limited by the radial distribution function spherical shells volume diverging with R^2 .

The *MP_tools* program suite [6] addresses these issues employing innovative algorithms. In the first case, recent developments of the non-uniform fast Fourier transform [7] permit to accelerate the summation of scattering amplitudes from large supercells by orders of magnitude, bring-

ing in the usual FFT speed and allowing for interactive work even in case of dynamic scattering functions $S(\mathbf{Q}, \omega)$ based on time sequences of thousands of frames. A similar effect in the PDF accumulation brings a Monte-Carlo algorithm with projective sampling [8], permitting to accumulate the $g(r)$ pair-distribution function with uniform (r -independent) accuracy without passing *via* the radial distribution function.

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