

**Experiment title:**Exploring Na–T–H systems ( $T = \text{Fe, Co}$ ) at extreme  $p, T$  in a large volume press: Search for new hydrogen-rich complex transition metal hydrides**Experiment****number:**

CH-5597

**Beamline:**

ID06-LVP

**Date of experiment:**

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**Date of report:**

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**Shifts:**

9

**Local contact(s):**

Kristina Spektor

*Received at ESRF:***Names and affiliations of applicants** (\* indicates experimentalists):**Kristina Spektor\*** (European Synchrotron Radiation Facility, Avenue des Martyrs 71, 38000 Grenoble, France)**Ulrich Häussermann\*** (Stockholm University, Department of Material and Environmental Chemistry (MMK), Svante Arrhenius vägen 16C, 10691 Stockholm, Sweden)**Andreas Fischer\*** (Augsburg University, Institute of Physics, 86135 Augsburg, Germany)**Report****1. Aim of the study**

The goal of the experiment CH-5597 was to search for the new hydrogen-rich complex transition metal hydrides (CTMH) in Na–T–H systems ( $T = \text{Fe, Co}$ ) at high pressures and temperatures. CTMH are a class of compounds with a general formula  $A_nTH_m$  ( $A$  is an alkali/alkaline earth metal,  $T$  is a Group IV–X transition metal). Their structures constitute  $TH_m^{n-}$  complexes, while  $A$  metals act as counterions. CTMH are actively studied as they display many remarkable properties, including hydrogen storage capability and superconductivity.<sup>1</sup> Despite an impressive range of existing compositions, CTMH combining first-row transition metals (TM) with monovalent counterions are very scarce and are mostly limited to lithium-balanced compounds.<sup>2,3</sup> At the same time, presence of alkali metal cations in the structure has a potential of stabilizing novel geometries of  $TH_m^{n-}$ , enhancing chances of reaching higher TM oxidation states and hydrogen content. Recent studies revealed a direct correlation of average counterion electronegativity ( $X_A$ ) with the stability of CTMH, with Li-containing representatives being at a lowest threshold.<sup>4</sup> As  $X_A$  for  $\text{Na}^+$  in hydrides exceeds that of  $\text{Li}^+$ , Na-stabilized CTMH with first-row TM are expected to be even more stable. Indeed, an unprecedented formation of a perovskite  $\text{NaNiH}_3$  was confirmed in our recent study, along with an array of hydrogen-rich  $\text{Na}_3\text{NiH}_5$  polymorphs.<sup>5</sup>

Performing hydrogenations at GPa pressures using large volume devices has already shown strong potential for accessing new CTMH structures.<sup>6,7</sup> Combining LVP technique with *in situ* diffraction is particularly advantageous, as it allows for efficient mapping of  $p, T$  space not only to search for new materials, but also to study their phase behaviour and optimize synthesis conditions for large scale production. ID06-LVP offers a unique opportunity to collect time-resolved angle-dispersive *in situ* PXRD during the reactions in multicomponent systems at GPa pressures while providing stable heating over a wide range of temperatures and sufficiently large sample volumes.<sup>8</sup> During CH-5597 we examined Na–T–H systems at ID06-LVP at target pressures of  $\sim 10$  GPa. Experimental details and results of the study are discussed below.

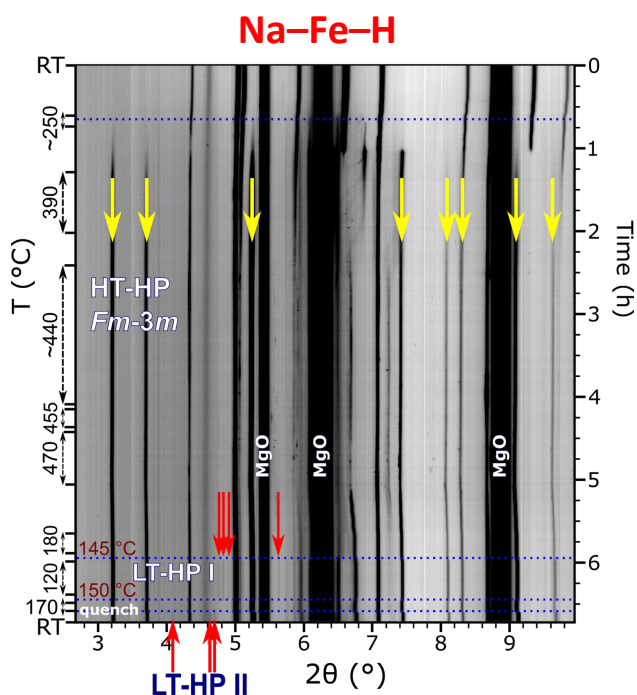
**2. Technical aspects**

Sample preparation was handled under argon in a glove box due to air- and moisture-sensitivity of the starting materials. Powders of sodium hydride (NaH) and transition metals (Fe, Co) were mixed in 2:1 molar ratio and pressed into pellets of 1.4 mm OD, 0.75 mm height. The samples were then sandwiched between 2

pellets of ammonia borane ( $\text{NH}_3\text{BH}_3$ ) hydrogen source and sealed inside NaCl capsules of 2.4 mm OD, 2.8 mm height. At target pressures,  $\text{NH}_3\text{BH}_3$  was expected to release hydrogen entirely at  $\sim 300$  °C, while its amount per sample provided roughly 5:1 H:T molar ratio during the experiment. NaCl was chosen as a capsule material for hydrogenation reactions as it is impermeable to  $\text{H}_2$  and creates a tight protective seal for highly sensitive materials. In addition, EOS of NaCl is well known, which allows to estimate  $p,T$  conditions during the experiment using *in situ* PXRD.

The samples were compressed and heated in a large volume press at ID06-LVP using 10/5 multianvil assemblies. The latter represented the downsized version of the 14/8 ones used during CH-4899 hydrogenation experiments. The major difference, however, was that the carbon foil heater material (0.5 mm thick) used in 14/8 assemblies was replaced with nickel metal foil ( $\sim 0.025$  mm thick) which allowed to preserve sufficient sample volume in a smaller 10/5 set up. In addition, in one of the runs 10/5 assembly was equipped with a type C thermocouple, providing power – T calibration for other experiments. Samples were pressurized to  $\sim 10$  GPa and heated using Delta Elektronika SM6000 power supply by regulating the power. Angle-dispersive PXRD patterns ( $\lambda=0.2296$  Å) were collected with a Detection Technology X-Scan series1 linear pixelated detector placed at an azimuth angle of  $270^\circ$ . During compression and decompression, a pattern would be saved each 32 seconds, while on heating collection speed was 3.2 sec/pattern. The speed and duration of the heating was adjusted based on the observed changes in the diffraction, and lasted up to 8 hours in order to drive the reactions to completion and study phase transition behaviour of the products. Heating was terminated either by temperature quenching or slow cooling, and the samples were further decompressed and recovered at ambient conditions for *ex situ* PXRD characterization.

### 3. Results and discussion



**Figure 1.** Compilation of PXRD data collected on heating in Na–Fe–H system at  $\sim 10$  GPa. Changes indicating formation of high pressure, high/low temperature polymorphs (HT-HP *fcc* phase and LT-HP, respectively) are marked by arrows.

reverted upon reheating. These changes were attributed to the transformation of the *fcc* structures into low temperature polymorphs. In case of Fe-containing sample, two low temperature phases were observed replacing one another during temperature variations, while formation of a single low temperature phase was noted in the system with cobalt. The structures observed at  $\sim 10$  GPa could not be preserved by decompression. Instead, both Na–T–H compounds underwent yet another transformation into low pressure polymorphs, which were recovered at ambient  $p,T$ . Extensive analysis of *ex situ* PXRD patterns of the ambient products collected at ID15B has established their isostructural relations to the known CTMH containing heavier metals of Groups VIII and IX –  $\text{Na}_3(\text{Ru/Os})\text{H}_7$ <sup>9</sup> and  $\text{Na}_3(\text{Rh/Ir})\text{H}_6$ .<sup>10</sup> Suggested analogous  $\text{Na}_3\text{FeH}_7$  and  $\text{Na}_3\text{CoH}_6$  structures were DFT-optimized, revealing both models to be highly energetically

Data collected during CH-5597 were thoroughly analyzed, and the extracted structural information was complemented by comprehensive DFT calculations and MD simulations. Overall, we have found that ternary Na–T–H ( $T = \text{Fe}, \text{Co}$ ) CTMH compounds were successfully produced in both Co- and Fe- containing systems upon heating at  $\sim 10$  GPa. Remarkably, synthesis of CTMH with given compositions has never been reported earlier. The compilation of PXRD patterns collected during the heating of the Na–Fe–H sample is shown as an example in Figure 1. The onset of the Na–T–H product formation was detected at  $\sim 250$  and  $\sim 170$  °C in the samples with Fe and Co metals, respectively. Analysis of *in situ* PXRD patterns revealed many similarities in the structures and phase behaviour of the new compounds. Above 300 °C the diffraction peaks of both Na–T–H phases were indexed to face-centered cubic unit cell with  $a$  parameter varying between 7 and 7.1 Å. Upon cooling as well as on temperature quench the peaks of the *fcc* structures underwent subtle yet noticeable changes (such as appearance of additional very faint reflections, peak broadening), which occurred instantaneously and could be

stable. The same Na:T:H stoichiometries were adopted for the high pressure polymorphs. The 3Na:1T arrangement in the high pressure, high temperature *fcc* structures was found to correspond to the one in Heusler alloys. MD simulations have shown that *fcc* phases are dynamically disordered, with  $\text{FeH}_7^{3-}$  and  $\text{CoH}_6^{3-}$  complex units undergoing reorientational dynamics. The formation of low temperature, high pressure polymorphs is interpreted as ordering of  $\text{TH}_m^n$  complexes on cooling, which results in slight displacements in 3Na:1T arrangements and likely leads to formation of superstructures. To obtain more detailed structural information for the high pressure polymorphs, further studies involving in situ neutron diffraction are intended.

The experiment CH-5597 at ID06-LVP was highly successful, as it led to the discovery of two unprecedented hydrogen-rich CTMH compounds,  $\text{Na}_3\text{FeH}_7$  and  $\text{Na}_3\text{CoH}_6$ , containing first row transition metals in unusually high oxidation states. The study has resulted in a manuscript, which is currently under review in *Inorganic Chemistry* journal.<sup>11</sup>

## References

- (1) Bronger, W. Synthesis and Structure of New Metal Hydrides. *Journal of Alloys and Compounds* **1995**, 229 (1), 1–9.
- (2) Sato, R.; Saitoh, H.; Endo, N.; Takagi, S.; Matsuo, M.; Aoki, K.; Orimo, S. Formation Process of Perovskite-Type Hydride  $\text{LiNiH}_3$ : In Situ Synchrotron Radiation X-Ray Diffraction Study. *Appl. Phys. Lett.* **2013**, 102 (9), 091901.
- (3) Saitoh, H.; Takagi, S.; Matsuo, M.; Iijima, Y.; Endo, N.; Aoki, K.; Orimo, S.  $\text{Li}_4\text{FeH}_6$ : Iron-Containing Complex Hydride with High Gravimetric Hydrogen Density. *APL Materials* **2014**, 2 (7), 076103.
- (4) D. Humphries, T.; A. Sheppard, D.; E. Buckley, C. Complex Transition Metal Hydrides: Linear Correlation of Countercation Electronegativity versus T–D Bond Lengths. *Chemical Communications* **2015**, 51 (56), 11248–11251.
- (5) Spektor, K.; Crichton, W. A.; Filippov, S.; Klarbring, J.; Simak, S. I.; Fischer, A.; Häussermann, U. Na–Ni–H Phase Formation at High Pressures and High Temperatures: Hydrido Complexes  $[\text{NiH}_5]^{3-}$  Versus the Perovskite  $\text{NaNiH}_3$ . *ACS Omega* **2020**, 5 (15), 8730–8743.
- (6) Takagi, S.; Iijima, Y.; Sato, T.; Saitoh, H.; Ikeda, K.; Otomo, T.; Miwa, K.; Ikeshoji, T.; Orimo, S. Formation of Novel Transition Metal Hydride Complexes with Ninefold Hydrogen Coordination. *Sci. Rep.* **2017**, 7, 44253.
- (7) Takagi, S.; Iijima, Y.; Sato, T.; Saitoh, H.; Ikeda, K.; Otomo, T.; Miwa, K.; Ikeshoji, T.; Aoki, K.; Orimo, S. True Boundary for the Formation of Homoleptic Transition-Metal Hydride Complexes. *Angew. Chem., Int. Ed.* **2015**, 54 (19), 5650–5653.
- (8) Guignard, J.; Crichton, W. A. The Large Volume Press Facility at ID06 Beamline of the European Synchrotron Radiation Facility as a High Pressure-High Temperature Deformation Apparatus. *Rev. Sci. Instrum.* **2015**, 86 (8), 085112.
- (9) Bronger, W.; Sommer, T.; Swinder, L.; Müller, P.  $\text{Na}_3\text{RuD}_7$  - Synthese und Struktur. *Zeitschrift für anorganische und allgemeine Chemie* **2001**, 627 (6), 1113–1114.
- (10) Bronger, W.; Gehlen, M.; Auffermann, G.  $\text{Na}_3\text{RhH}_6$ ,  $\text{Na}_3\text{IrH}_6$  und  $\text{Li}_3\text{IrH}_6$ , neue komplexe Hydride mit isolierten  $[\text{RhH}_6]^{3-}$  und  $[\text{IrH}_6]^{3-}$ -Oktaedern. *J. Alloys Compd.* **1991**, 176 (2), 255–262.
- (11) Spektor, K.; Crichton, W. A.; Filippov, S.; Simak, S. I.; Fischer, A.; Häussermann, U.  $\text{Na}_3\text{FeH}_7$  and  $\text{Na}_3\text{CoH}_6$ : Hydrogen-rich first-row transition metal hydrides from high pressure synthesis. *Inorg. Chem.* **2020** (submitted, manuscript under review).