Na\textsubscript{3}FeH\textsubscript{7} and Na\textsubscript{3}CoH\textsubscript{6}: Hydrogen-Rich First-Row Transition Metal Hydrides from High Pressure Synthesis

Kristina Spektor, Wilson A. Crichton, Stanislav Filippov, Sergei I. Simak, Andreas Fischer, and Ulrich Häussermann*

**ABSTRACT:** The formation of ternary hydrogen-rich hydrides involving the first-row transition metals TM = Fe and Co in high oxidation states is demonstrated from in situ synchrotron diffraction studies of reaction mixtures NaH−TM−H\textsubscript{2} at p ≈ 10 GPa. Na\textsubscript{3}FeH\textsubscript{7} and Na\textsubscript{3}CoH\textsubscript{6} feature pentagonal bipyramidal Fe\textsubscript{4+} and octahedral Co\textsubscript{4+} 18-electron complexes, respectively. At high pressure, high temperature (300 < T ≤ 470 °C) conditions, metal atoms are arranged as the face-centered cubic Heusler structure, and ab initio molecular dynamics simulations suggest that the complexes undergo reorientational dynamics. Upon cooling, subtle changes in the diffraction patterns evidence reversible and rapid phase transitions associated with ordering of the complexes. During decompression, Na\textsubscript{3}FeH\textsubscript{7} and Na\textsubscript{3}CoH\textsubscript{6} transform to tetragonal and orthorhombic low pressure forms, respectively, which can be retained at ambient pressure. The discovery of Na\textsubscript{3}FeH\textsubscript{7} and Na\textsubscript{3}CoH\textsubscript{6} establishes a consecutive series of homelectic hydrogen-rich complexes for first-row transition metals from Cr to Ni.

1. INTRODUCTION

Expectations for high temperature superconductivity have stimulated intensive research efforts into binary metal–H systems at high pressures, which have resulted in the discovery of unprecedented hydrogen-rich hydrides.\textsuperscript{1–4} These hydrides, also called super- or polyhydrides, exhibit stunning compositions and hydrogen structures, which include clathrate-like cages (as in LaH\textsubscript{0.9}CaH\textsubscript{0.1}),\textsuperscript{5–7} oligomeric chain fragments (as in NaH\textsubscript{0.86}),\textsuperscript{8} and two-dimensional layers (as in FeH\textsubscript{5}).\textsuperscript{9} High temperature superconductivity approaching room temperature has been predicted for alkaline earth, La, and Y hydrides with clathrate-like structures and was recently experimentally confirmed for LaH\textsubscript{0.9}\textsuperscript{10}

An important issue is that binary superhydrides and their interesting properties can only be observed at extreme pressures in the Mbar range (i.e., around 100 GPa). Upon pressure release, they decompose into ordinary metal hydrides and hydrogen. The situation may be different with ternary hydrides because decomposition pathways are expected to be more complex, which increases the likelihood of trapping metastable superhydride phases. Also, ternary hydrogen-rich hydrides may form at much lower pressure conditions. Indeed, it has been recently shown that the application of modest pressures of around 5 GPa can already afford new hydrogen-rich complex transition metal hydrides, CTMHs, in which group 4–6 metals attain unusually high H coordination numbers. These new CTMHs comprise homelectic complex ions like CrH\textsubscript{7}, NbH\textsubscript{9}, and Ti\textsubscript{2}H\textsubscript{14} and are semiconductors.\textsuperscript{11–14} Yet, they are recoverable to ambient pressure, and doping with hole carriers has been suggested to achieve superconductivity.\textsuperscript{14} Here, we demonstrate the accessibility of hydrogen-rich CTMHs in the Na−Fe−H and Na−Co−H systems by using pressures around 10 GPa and slightly elevated temperatures up to 470 °C. We argue that the obtained compounds establish a consecutive series of homelectic hydrogen-rich complexes for first-row transition metals from Cr to Ni.

There are hitherto no ternary Na−Fe−H and Na−Co−H compounds reported, which is in contrast with the heavier group 8 and 9 congeners. Na\textsubscript{14}RhH\textsubscript{6}/Na\textsubscript{14}IrH\textsubscript{6} and Na\textsubscript{14}RuH\textsubscript{5}/Na\textsubscript{14}OsH\textsubscript{5} can be prepared when heating mixtures of NaH and transition metal in a (pressurized) hydrogen atmosphere using stainless steel autoclaves.\textsuperscript{15,16} Attainable pressures in such devices are typically restricted to a few kbar (~0.3 GPa).\textsuperscript{17} Large volume presses (LVPs) allow for pressures much in
excess of 10 GPa and can provide well-controlled $p,T$ environments for high pressure hydrogenation reactions. LVP hydrogenations utilize an internal hydrogen source and are performed in NaCl capsules, which offer tight seals and withstand H diffusion. Ammonia borane, BH$_3$NH$_3$, which decomposes neatly into inert BN and H$_2$ at comparatively low temperatures ($200–300^\circ$C), has been proven an ideal internal H source. In situ studies of hydrogenations at pressures up to 12 GPa have been recently facilitated at the beamline ID06-LVP, ESRF.

2. EXPERIMENTAL SECTION

The samples for the high pressure hydrogenation experiments were prepared in an Ar filled glovebox. NaH (Sigma-Aldrich, 90%) and powdered transition metals TM (TM = Fe, Co (ABCR, 99.999%)) were thoroughly mixed at a molar ratio of 2:1 (NaH:TM) and then powdered transition metals TM (TM = Fe, Co (ABCR, 99.999%)) decomposes neatly into inert BN and H$_2$ at comparatively low temperatures ($200–300^\circ$C), has been proven an ideal internal H source. In situ studies of hydrogenations at pressures up to 12 GPa have been recently facilitated at the beamline ID06-LVP, ESRF.

High pressure experiments were performed at beamline ID06-LVP, ESRF (Grenoble) using 10/5 multianvil assemblies. The setup is sketched in Figure S1. The sample capsules, protected by 2.85 mm OD BN sleeves, were inserted into 10 mm OEL Cr-doped MgO octahedra, along with two 2.85 mm OD ZrO$_2$ plugs and a nickel foil furnace (2.9 mm OD). Two millimeter OD circular windows were cut along the beam direction in the octahedra and the amorphous SiBCN rods and 5 mm wide MgO rectangles were used as X-ray windows along the beam direction in the octahedra and the gaskets, respectively. Initially, the assemblies were compressed at rates of 0.5 bar/min (2.6–2.9 GPa/h) and, after reaching 20 bar oil pressure, the compression proceeded at a rate of 1 bar/min (3.3–3.5 GPa/h). At target pressure, the samples were heated. The heating rates varied between 9–12 °C/min at $T <$ 300 °C and 4–5 °C/min at $T >$ 400 °C. Pressure was estimated from PXRD diffraction patterns using the NaCl equation of state. In the Na–Fe–H experiment, the assembly was equipped with a type C W–Re thermocouple (see Figure S1). The extracted power–temperature data were utilized to evaluate the temperatures in the Na–Co–H run.

Angle-dispersive powder X-ray diffraction patterns were collected continuously over a 2.05–10.5° 2θ range at a constant wavelength (0.2296 Å). A Detection Technology X-Scan series1 linear pixilated detector was used for data acquisition. A diffraction data set was typically saved every 32 s during compression and decompression and every 3.2 s during heating. Calibration was performed using a mixture of LaB$_6$ (NIST SRM 660a) and Si (NIST SRM 640e) powders. The in situ data were integrated, manipulated, and visualized using the Fit2D software.

Products of the high pressure experiments were recovered at ambient conditions in the glovebox and sealed inside glass capillaries for ex situ PXRD characterization. PXRD patterns of recovered samples were collected at the ID15B beamline at the ESRF. The measurements were performed at a monochromatic wavelength of 0.41112 Å with the beam focused to 30 × 30 µm size on the sample and diffraction data was acquired on a Mar555 flat-panel detector. The integration of 2D data was performed using the Fit2D software.

Le Bail analysis and Rietveld refinement procedures were used in situ and ex situ PXRD data were performed with the Jana2006 software. In situ diffraction data were optimized by averaging 20–50 patterns collected during the temperature dwell to improve signal-to-noise ratio and minimize any possible texture contribution. All patterns were corrected for background prior to the analysis by subtracting the minimal value of observed intensity from the $I_{obs}$ column. For peak shape fitting a pseudo-Voigt function was used.

DFT enthalpy calculations were performed using the Vienna Ab Initio Simulation Package (VASP) in the framework of the projector augmented wave method (PAW) within generalized gradient approximation (GGA), and employing the Perdew–Burke–Ernzerhof (PBE) parameterization of the exchange-correlation functional. The cutoff energy for the plane wave basis set was 500 eV for all simulations. Structural relaxations employed a 4 × 4 × 4 Monkhorst–Pack (MP) $\Gamma$-point grid for Pnma LP Na$_3$CoH$_6$ ($Z = 4$) and a 4 × 4 × 8 grid for P4$_{2}$$\bar{1}$2$_{1}$m LP Na$_3$FeH$_7$ ($Z = 4$). For the Z$=$ 32 super cell modeling of LT-HP Na$_3$CoH$_6$ phases only the $\Gamma$-point (1 × 1 × 1) was considered. For the relaxations, total energies were converged to better than 10$^{-4}$ eV. Total energy calculations were carried out using the tetrahedron method with Blöchl correction on the same k-point.
Hoover thermostat at 300 and 1000 K. The simulation cell was a 2 × 2 × 2 supercell and the 0.8 (TM = Fe, Co) were employed, i.e. the TM:H ratio was 1:~2.5. In the following, we describe in situ LVP hydrogenation experiments, compiled in Figure 1, during which hydride formation and phase transitions at high pressure, high temperature conditions were examined in great detail.

The samples were heated at a starting pressure of ~10 GPa. Weak reflection lines indicating the formation of ternary hydride phases became visible at temperatures around 200 °C. As later described, these ternary hydride phases possess a metal composition 3Na:TM:BH(3−x) with x = 2 and 3. The inspection of peak positions and corresponding temperature/pressure manipulations are provided in the Supporting Information (text and Figures S2–S5).

To conclude the experiments, the samples were decompressed at room temperature and subsequently recovered. The residual pressure at the end of the decomposition was ~1.9 GPa and ~0.7 GPa for the Na−Fe−H and Na−Co−H samples, respectively. During decompression, the diffraction patterns remained unchanged, apart from obvious lattice expansion. However, the patterns of the recovered samples at ambient pressure were radically different compared to the in situ data. Accordingly, LT-HP Na3(TM)H6 underwent either decomposition or transformation to an ambient pressure form, LP Na3(TM)H6. The inspection of peak positions and intensities of integrated 2-dimensional synchrotron PXRD data pointed strongly to isosstructural relations with Na3Ru/OsH6 (space group P43/mmm (136)) and Na3Ru/IrH6 (space group Pmnn (62)) for the Na−Fe−H and Na−Co−H products, respectively. Patterns were then examined via Le Bail analysis and structure solution using the Superflip grids. Electronic density of states (DOS) calculations used the VASP parameters RWIGS: Na = 1.4, Fe/Co = 0.8, and H = 1.1 Å. The phonon dispersions and the phonon partial DOS were calculated on 2 × 2 × 2 MP k-point grids using the small displacement method as implemented in Phonopy. Total energies were converged better than 10−5 eV. The ionic positions were relaxed before the phonon calculations. Ab initio MD (AIMD) simulations of cubic HT-HP Na3(TM)H6 in the NVT ensemble (i.e., maintaining the number of atoms N, volume of the system V, and temperature T) were performed using the Nosé–Hoover thermostat at 300 and 1000 K. V corresponded to the experimental volumes observed at ~10 GPa (a = 7.09 Å (360 °C), Na−Fe−H) and 7.04 Å (420 °C, Na−Co−H) for the 1000 K simulations and was slightly compressed for the 300 K simulations. The simulation cell was a 2 × 2 × 2 supercell (Z = 32) of the Γ-point.

3. RESULTS AND DISCUSSION

During this study, reaction mixtures NaH:TM:BH2NH3:2:1−0.8 (TM = Fe, Co) were employed, i.e. the TM:H ratio was 1:~2.5. In the following, we describe in situ LVP hydrogenation experiments, compiled in Figure 1, during which hydride formation and phase transitions at high pressure, high temperature conditions were examined in great detail.

The samples were heated at a starting pressure of ~10 GPa. Weak reflection lines indicating the formation of ternary hydride phases became visible at temperatures around 200 °C. As later described, these ternary hydride phases possess a metal composition 3Na:TM:BH2NH3 (despite the 2:1 NaH:TM ratio of the reaction mixtures) and are denoted in the following as HT-HP Na3(TM)H6. The diffraction lines from HT-HP Na3(TM)H6 became more pronounced during a subsequent alteration of heating and temperature dwells performed to aid the completion of ternary phase formation. The highest temperatures applied were 470 and 420 °C for TM = Fe and Co, respectively. The diffraction peaks from HT-HP Na3(TM)H6 were indexed to an fcc lattice, with a varying between 7.08−7.12 Å and 7.00−7.05 Å for TM = Fe and Co, respectively, during the course of the heating and temperature dwells.

Afterward, the samples were slowly cooled, and during cooling, sets of additional, very weak reflections appeared in the PXRD patterns, indicating transformations to low temperature forms (LT-HP Na3(TM)H6). LT-HP Na3(TM)H6 was seen below 300 °C. For Na3FeH6, two LT-HP phases formed upon cooling, evidenced by two distinct sets of additional weak reflections: the first below 150 °C and the second at ~90 °C. These sets were observed to replace one another during heating−cooling cycles. In both systems, the HT-to-LT transitions appeared reversible. The weak reflections instantaneously disappeared after reheating the samples. At the same time, the HT-HP forms could not be preserved by temperature quenching. The detailed descriptions of the in situ experiments and corresponding temperature/pressure manipulations are provided in the Supporting Information (text and Figures S2–S5).

Figure 2. The structures of tetragonal LP Na3FeH7 (left) and orthorhombic LP Na3CoH6 (right) are shown. (a) P43/mnm structure of LP Na3FeH7 and Pnma structure of LP Na3CoH6 according to DFT optimization. Na ions are depicted as golden circles, and complexes of (TM)H3− are depicted as green polyhedra. (b) Local coordination of (TM)H3− complexes by 8 Na cations (distorted cube) and structure of (TM)H3− complexes. Na, Ni, and H atoms are depicted as golden, green, and gray circles, respectively. Interatomic TM−H distances are indicated (in Å). (c) Arrangement of distorted Na8 cubes (blue polyhedra) in the LP structures. The central building unit is a pair of edge-condensed distorted cubes (highlighted with a darker color). (d) Z = 32 MD snapshot of HT-HP Na3FeH7 and Na3CoH6 at 1000 K after equilibration. (TM)H3− complexes are drawn as green polyhedra.
algorithm\textsuperscript{30} yielded metal arrangements with composition 3Na:1TM, for which Wyckoff positions of the atoms coincided with those of the Na\textsubscript{3}OsH\textsubscript{5}− and Na\textsubscript{3}IrH\textsubscript{6}− type structures.

To confirm the isostructural relation between LP Na\textsubscript{3}(TM)H\textsubscript{6} and the Na\textsubscript{3}OsH\textsubscript{5} and Na\textsubscript{3}IrH\textsubscript{6} types, DFT optimization of the LP structures was performed using the H atom arrangement in Na\textsubscript{3}OsH\textsubscript{5} and Na\textsubscript{3}IrH\textsubscript{6}. The lattice parameters of the computed equilibrium structures agreed closely with those extracted from the Le Bail fits of the PXRD data. The DFT-optimized LP Na\textsubscript{3}FeH\textsubscript{7} and Na\textsubscript{3}CoH\textsubscript{6} structures (which are presented in Tables S1 and S2) were then used as an input for a final Rietveld refinement against experimental PXRD data, which resulted in remarkably close fits ($R_{\text{obs}} = 2.61$ and 2.30\%, respectively). Fractional coordinates and atomic displacement parameters of H atoms were constrained during the refinement. Rietveld plots and crystallographic data are provided in the Supporting Information (Figure S7, Tables S3 and S4), along with a description of refinement strategies.

The structures of tetragonal LP Na\textsubscript{3}FeH\textsubscript{7} and orthorhombic LP Na\textsubscript{3}CoH\textsubscript{6} are shown in Figures 2a−c-left and a−c-right, respectively. They are built from homoleptic pentagonal bipyramidal FeH\textsubscript{5}− and octahedral CoH\textsubscript{6}− complexes. Fe−H distances to equatorial ligands are between 1.52 and 1.55 Å, whereas distances to apical ligands are elongated at 1.62 Å. The Co−H distances are in a narrow range of 1.53−1.57 Å and similar to the equatorial Fe−H distances. The structures share a common building principle in that complexes are surrounded by distorted cubes of Na ions (Figures 2b-left and b-right). The distorted Na\textsubscript{4} cubes are then arranged as pairs by sharing a common edge, and pairs of edge-condensed cubes are connected via shared corners to yield the 3D crystal structure (Figures 2c-left and c-right).

The HT-HP forms were assumed to possess the stoichiometry of the LP phases and also to be built from FeH\textsubscript{5}− and octahedral CoH\textsubscript{6}− complexes. The in situ PXRD patterns were analyzed using Le Bail fits with the space group Fm\textit{3}m (225). Space group and reflection intensities in combination with the 3:1 Na:TM composition of the phases invariably pointed to an Fm\textit{3}m stoichiometry of the HT-HP systems as extracted from DFT total energy calculations (referring to absolute zero). Formation enthalpies of both LP phases were calculated with respect to NaH, TM, and H\textsubscript{2}. The HT-HP model corresponded to MD snapshots which were relaxed in the considered volume range. The equilibrium volumes of the HT-HP phases are by about 10\% smaller than the LP counterparts (cf. Figure S9). The $\Delta H$−$p$ relations suggest that below 4 GPa, the LP phases are more stable than the disordered cubic HT-HP ones. It is important to point out that formation enthalpies of both LP phases are largely negative. This implies that these phases actually do not require high pressures for thermodynamic stabilization. However, the synthesis of Na\textsubscript{3}FeH\textsubscript{7} and Na\textsubscript{3}CoH\textsubscript{6} requires high pressures because with pressure the decomposition temperature will increase, thus enabling the application of elevated temperatures for initiating the formation reactions. Additionally, high pressures will improve the kinetics of the heterogenous reaction between NaH and TM particles.

The electronic structures of Na\textsubscript{3}FeH\textsubscript{7} and Na\textsubscript{3}CoH\textsubscript{6} conform to the picture of stable 18-electron complexes. The occupied states in the electronic density of states (DOS) mirror the MOs (and crystal field splitting) of isolated, idealized, pentagonal bipyramidal D\textsubscript{5h} and octahedral O\textsubscript{h} complexes (Figure S16). The calculated band gaps are 1.5 and 2 eV for LP Na\textsubscript{3}FeH\textsubscript{7} and Na\textsubscript{3}CoH\textsubscript{6}, respectively. The phonon DOS for LP Na\textsubscript{3}FeH\textsubscript{7} and Na\textsubscript{3}CoH\textsubscript{6} as shown in Figure S17, predict the stretching modes of FeH\textsubscript{5}− in a range 1400−2000 cm\textsuperscript{−1}, which is at slightly higher wavenumbers compared to CrH\textsubscript{5}− present in Mg\textsubscript{2}CrH\textsubscript{6} (1450−1650 cm\textsuperscript{−1}).\textsuperscript{11} This indicates stronger Fe−H bonds as also reflected in the interatomic distances ($d$(Cr−H) = 1.67 Å vs $d$(Fe−H) = 1.56 Å). The stretching modes of CoH\textsubscript{6}− are in the range...
Conventional autoclave-based synthesis, using pressurized H$_2$ gas up to 150 kbar, affords—primarily as Mg compounds—tetrahedral d$^5$ Mn(II)H$_4^{2-}$, octahedral d$^6$ Fe(II)H$_6^{2-}$, two forms of Co complexes (saddle-shaped d$^{10}$ Co(-I)H$_4^{2-}$ and square pyramidal d$^9$ Co(I)H$_5^{3-}$), as well as tetrahedral d$^{10}$ Ni(0)H$_4^{2-}$. Unsuccessful attempts to produce CTMHs with TMs to the left from Mn by conventional techniques gave rise to the perception that such complexes cannot exist with more electron-poor TMs. The recent discovery of Mg$_2$CrH$_6$ showed that this boundary can be crossed with the application of gigapascal pressures and established at the same time Cr(II)H$_5^{3-}$ as the first hydrogen-rich complex for first-row transition metals.$^{14}$ Through use of Na as the counterion, hydrogen-rich complexes of the later first-row transition metals based on increased oxidation states can be achieved, i.e. Fe(IV)H$_7^{3-}$ and Co(III)H$_6^{3-}$, and, as recently shown, also Ni(II)H$_5^{3-}$. Note that the oxidation state for Fe in FeH$_7^{3-}$ is remarkably high in conjunction with a H ligand environment. An earlier theoretical work predicted that also Li$_3$FeH$_7$ may be accessible, but this compound has not yet been synthesized.$^{45}$ Finally, Mn represents a special case. Earliest application of gigapascal pressures, $\sim$2 GPa, afforded Mg$_2$MnH$_6$ with octahedral d$^8$ Mn(III)H$_6^{3-}$ complexes. However, we infer that when using Na as the counterion (and higher pressures), it should be possible to also synthesize Na$_3$MnH$_6$ possibly with the K$_2$ReH$_6$ structure.$^{43}$ Octahedral d$^9$ Mn(III)H$_6^{2-}$ complexes would represent the “true” member in a consecutive series of hydrogen-rich complexes in which the first-row TM carries the possibly highest attainable oxidation state.

### 4. CONCLUSIONS

It has been shown that the application of pressures in the gigapascal range systematically extends CTMHs for first-row transition metals by affording higher oxidation states for TMs, i.e. Fe(IV), Co(III), and Ni(II). Highly remarkable is also the recently reported binuclear complex Ti$_2$H$_{14}^{6-}$ in quaternary BaCa$_2$Ti$_2$H$_{10}$, which was obtained from high pressure synthesis at 4 GPa.$^{14}$ Ti$_2$H$_{14}^{6-}$ is composed of two face-sharing monocapped square antiprisms and features Ti in the oxidation state IV. More surprising discoveries of multinary hydrogen-rich hydrides can be expected, eventually also yielding ambient pressure recoverable superconductors. In this respect, LVP hydrogenations provide excellent opportunities for controlled synthesis of sizable quantities using pressures up to 15 GPa.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c02294.

Descriptions of in situ PXRD experiments, structural investigations, refinement strategies, and results from theoretical calculations; sketch of the 10/5 multianvil assembly; plots of temperature variations as a function of time; PXRD patterns showing temperature-induced phase transitions; Rietveld plots and refinements; total energy vs volume relations; diagonal and nondiagonal components of the stress tensor as a function of simulation time; 2D histograms of angular positions of H atoms in the HT-HP phases from AIMA simulations; time-dependent variation of bond angles in the HT-HP phases; electronic DOS for the LP phases; pDOS for the LP phases; crystallographic data (PDF)

### Accession Codes

CCDC 2022756–2022759 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

### AUTHOR INFORMATION

#### Corresponding Authors

Kristina Spektor — ESRF, The European Synchrotron Radiation Facility, F-38000 Grenoble, France; orcid.org/0000-0002-3267-9797; Email: Kristina.Spektor@gmail.com

Ulrich Häussermann — Department of Materials and Environmental Chemistry, Stockholm University, SE-10691 Stockholm, Sweden; orcid.org/0000-0003-2001-4410; Email: Ulrich.Hausermann@mmk.su.se

#### Authors

Wilson A. Crichton — ESRF, The European Synchrotron Radiation Facility, F-38000 Grenoble, France

Stanislav Filippov — Theoretical Physics Division, Department of Physics, Chemistry and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden; Department of Materials and Environmental Chemistry, Stockholm University, SE-10691 Stockholm, Sweden

Sergei I. Simak — Theoretical Physics Division, Department of Physics, Chemistry and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden

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1. Filippov, S. I.; Simak, S. I.; Crichton, W. A.; Haussermann, U.; Spektor, K. Theoretical Physics Division, Department of Physics, Chemistry and Biology, Linköping University, SE-581 83 Linköping, Sweden; Environmental Chemistry, Stockholm University, SE-10691 Stockholm, Sweden; Facilitie, F-38000 Grenoble, France; ESRF, The European Synchrotron Radiation Facility, F-38000 Grenoble, France. Inorg. Chem. 2020, 59, 16467–16473.
Inorganic Chemistry

Andreas Fischer — Department of Physics, Augsburg University, D-86135 Augsburg, Germany

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.0c02294

Notes
The authors declare no competing financial interest.

Acknowledgments

The ESRF is thanked for allocating the beamtime CH-5597 at beamline ID06-LVP. K.S. would like to thank Michael Hanfland for the help with measurements at beamline ID15B and Harald Müller for assistance with the Chemistry Laboratory facilities at ESRF. S.I.S. acknowledges support from the Swedish Government Strategic Area Grant in Materials Science on Functional Materials at Linköping University (Faculty Grant SFO-Mat-LIU No. 2009 00971). S.F. acknowledges the financial support from Carl Tryggers Stiftelse (CTS) for Vetenskaplig Forsknings through grants 16:198 and 17:206. The computations were performed using resources provided by the Swedish National Infrastructure for Computing (SNIC) at the High Performance Computing Center North (HPC2N).

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