

Experimental report

30/07/2025

Proposal: EASY-1179

Council: 4/2023

Title: Hydride-ion dynamics in the nitride-hydride $\text{Ca}_3\text{CrN}_3\text{H}$

Research area: Materials

This proposal is a new proposal

Main proposer: Lucas FINE

Experimental team:

Local contacts: Monica JIMENEZ RUIZ

Samples: $\text{Ca}_3\text{CrN}_3\text{H}$

Instrument	Requested days	Allocated days	From	To
IN1	12	12	27/08/2023	28/08/2023

Abstract:

Topochemical reactions have recently led to great progress in the discovery of new metastable compounds with novel chemical and physical properties. A primary example is the recent discovery of hexagonal calcium chromium nitride-hydride $\text{Ca}_3\text{CrN}_3\text{H}$. Recently, we investigated the nature of hydride-ion dynamics in $\text{Ca}_3\text{CrN}_3\text{H}$, by using quasielastic neutron scattering (QENS). The experiments revealed the presence of diffusive motions of the hydride-ions, featured by a characteristic time-scale of about 10 picoseconds. Interestingly, the dynamics change drastically at $T=250$ K: the long-range translational motions observed at lower temperatures become localized. In order to elucidate the origin of this evolution, we propose to perform a temperature-dependent inelastic neutron scattering experiment in the range 0-300 K. Crucially, observing the temperature dependence of the vibrational modes of the hydrogen species will inform us about the evolution of their local coordination environment, and thus help to understand the QENS data. We propose to use the spectrometer LAGRANGE to measure the hydrogen vibrational modes in the range 80-120 meV over the temperature range 0-300 K.

Hydride-ion dynamics in the nitride-hydride $\text{Ca}_3\text{CrN}_3\text{H}$

Proposal EASY-1179 - August 2023

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1 Introduction

The novel nitride-hydride $\text{Ca}_3\text{CrN}_3\text{H}$ is a promising candidate for applications in, e.g., catalysis [1]. However, given the recent discovery of this material, little is still known about its local structure and dynamics. Recently, we investigated the nature of hydride-ion dynamics using the technique quasielastic neutron scattering (QENS). A key result was the observation of hydride-ion diffusion in $\text{Ca}_3\text{CrN}_3\text{H}$. In to get more detailed information about the mechanism of the diffusion, it is essential to have detailed information about the local coordination of hydride-ions in this material. For this purpose, this inelastic neutron scattering study aims to measure the vibrational spectrum of hydrides-ions in $\text{Ca}_3\text{CrN}_3\text{H}$. This experiment was conducted at IN1-LAGRANGE.

Approximately 1.3 g of $\text{Ca}_3\text{CrN}_3\text{H}$ powder sample synthesized by collaborators at Kyoto University were inserted into cylindrical aluminum cells and sealed with stainless steel metal rings inside a He-filled glovebox. Spectra were acquired at temperatures between 300 and 7 K with the Si(111), Si(311), and Cu(220) monochromators, giving access to an energy window of 4.5–500 meV. The data reduction was done within Mantid and included a normalization to monitor counts and an empty cell subtraction.

2 Results

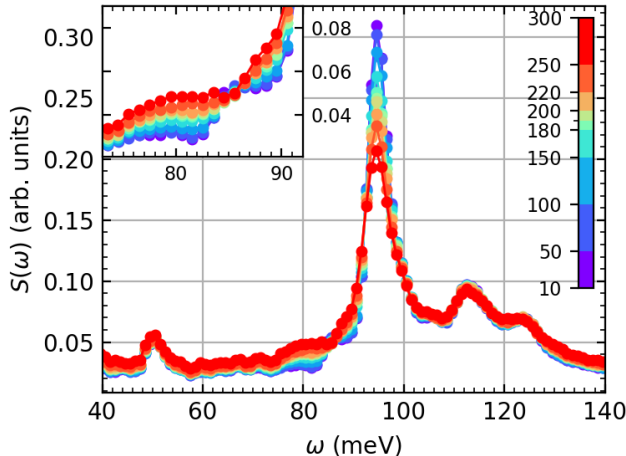


Figure 1: $S(\omega)$ of the hydride-ion vibrational modes in $\text{Ca}_3\text{CrN}_3\text{H}$ as measured on IN1-LAGRANGE.

As shown in Figure 1, the spectra are characterized by an intense peak at ~ 95 meV, as well as peaks of smaller intensity at ~ 50 , ~ 80 , ~ 115 , and ~ 123 meV. These peaks were assigned to hydride-ion vibrational modes, based on density functional theory (DFT) calculations. The notable temperature dependence of the peak at ~ 95 meV was attributed to the anharmonic behavior of the associated mode. More information about this experiment can be found in the published article ref. [2].

References

- [1] Cao, Y. et al. Topochemical Synthesis of $\text{Ca}_3\text{CrN}_3\text{H}$ Involving a Rotational Structural Transformation for Catalytic Ammonia Synthesis. *Angewandte Chemie International Edition* **2022**, *n/a*.
- [2] Fine, L.; Lavén, R.; Wei, Z.; Tsumori, T.; Kageyama, H.; Kajimoto, R.; Jimenez-Ruiz, M.; Koza, M. M.; Karlsson, M. Configuration and Dynamics of Hydride Ions in the Nitride-Hydride Catalyst $\text{Ca}_3\text{CrN}_3\text{H}$. *Chemistry of Materials* **2025**, *37*, 489–496.