Neutron Vibrational Spectroscopic Evidence for Short H···H Contacts in the $R\text{NiInH}_{x}$ Metal Hydride

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Hydrogen is emerging as an important alternative energy carrier to carbon-based fuels. A key hurdle impeding the widespread adaptation of hydrogen as a fuel is the lack of suitable hydrogen storage materials [1, 2]. One promising class of hydrogen storage materials which may be useful for long-term, stationary storage of hydrogen is the metal hydrides [3]. These compounds are typically alloys that chemisorb the hydrogen—they break the H–H bond at the surface of the material and the hydrogen is stored as hydride ions in the interstitial sites in the metal lattice. Metal hydrides can reach extremely high volumetric storage capacities; however, the storage capacity is fundamentally limited by coulombic repulsion of the hydride ions, and new materials with enhanced storage capacities are still needed. An empirical closest H···H distance of $\approx 2$ Å has been found in metal hydrides, which is known as the Switendick-Westlake criterion. Very few materials violate this empirical rule. Studying these materials to develop an understanding of the mechanism enabling the violation of this criterion may be a path forwards for designing new metal hydrides with greatly enhanced storage capacities. Of the compounds that do violate the Switendick-Westlake criterion, perhaps the best studied is the family of $R\text{NiInH}_x$ compounds, $R = \text{La, Ce, Nd, and Pr}$ [4, 5]. Neutron diffraction measurements revealed that, at $x > \frac{2}{3}$, hydride ions occupy adjacent crystallographic sites with an H···H distance of $\approx 1.6$ Å, in violation of the Switendick-Westlake criterion (Figure 1). However, there were no neutron vibrational spectroscopic investigations of the signatures of close H···H contacts in these metal hydrides to date.

A team of researchers—with members from the NIST Center for Neutron Research (NCNR), Oak Ridge National Laboratory (ORNL), and the Institute for Energy Technology (Kjeller, Norway)—investigated the neutron vibrational spectroscopic signatures of close H···H contacts in the $R\text{NiInH}_x$ metal hydrides [6]. The researchers combined neutron vibrational spectroscopy (NVS) measurements with density functional theory calculations to study the chemical bonding in the metal hydrides $R\text{NiInH}_x$ ($R = \text{La, x = 1.6; Ce, x = 1.4}$). The NVS measurements were conducted using the BT-4 Filter Analyzer Neutron Spectrometer (FANS) at the NCNR and the high-resolution broadband TOSCA spectrometer at the pulsed neutron source of ISIS at the Rutherford-Appleton Laboratory in Chilton, the United Kingdom.

First, several compounds which do not violate the Switendick-Westlake criterion were measured as controls in this study. These included LaNiInH$_{0.67}$ and a new family of structurally similar and chemically analo-
gous materials, CeNiSnH, CeNiSnH₂, and CeNiSnD₂ were structurally characterized using powder neutron diffraction measurements conducted at the R2 Reactor at the Studsvik Neutron Research Laboratory, Uppsala, Sweden in addition to the NVS measurements. These compounds contain the same crystallographic, interstitial sites as CeNiInH₁₄. However, the near-neighbor sites are not simultaneously occupied even at the high hydride concentration of \( x = 2 \). Similarly, for LaNiInH₀.₆₇, the hydride concentration is sufficiently low such that the near-neighbor sites are not simultaneously occupied, and the Switendick-Westlake criterion is not violated in this material. As such, the NV spectra for these compounds do not display any abnormal features. In the range of 40 meV to 160 meV, the researchers observed the typical metal–hydride bending and stretching modes, as expected (Figure 2, top).

The team then conducted the NVS measurements for LaNiInH₁.₆ and CeNiInH₁.₄ (Figure 2, middle and bottom). They observed significant shifts in the spectral features for the metal–hydride stretching and bending modes. The DFT calculated phonon density of states was used to simulate the NV spectra. Using these calculations, the researchers generated animations illustrating the atomic motion corresponding to each observed feature in the neutron vibrational spectra. These animations greatly facilitated the mode assignments in the spectra. The researchers found that the close H···H contacts lead to softening and further splitting of the Ni–H bending and rocking modes. By coupling NVS experiments with DFT calculations, the researchers showed the spectral signatures of close H···H contacts in the \( \text{RNiInH}_x \) family of metal hydrides.

The experiments and theory corroborated a previously hypothesized mechanism thought to enable close H···H contacts in these compounds. The previous hypothesis cited effective screening of the hydride charges by the \( R_3 \) faces. The researchers here showed spectroscopic evidence which supports this hypothesis—they observed significant softening and further splitting of the modes associated with the close H atoms. This experimental insight into the mechanism enabling the viola-
The application of the Switendick-Westlake criterion may be useful in the future for designing new materials with enhanced hydrogen storage capacities for applications in stationary hydrogen storage.

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