



	Experiment title: Electronic structure and hydrogen storage in lithium tetrahydroborate	Experiment number: HE-2449
Beamline: ID16	Date of experiment: from: 14.06.2007 to: 19.06.2007	Date of report:
Shifts: 15	Local contact(s): Dr. S. Huotari	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): K. Hämäläinen*, S. Galambosi*, A. Mattila* Division of Materials Physics, Department of Physics, POB 64, 00014 University of Helsinki, Finland		

Report:

Among metal hybrids lithium tetraborohydride (LiBH_4) is one of the most promising candidates for reversible, solid state hydrogen storage [1]. Due to the light elements Li and B, it has a large hydrogen content of 18.5 wt.%. Technologically the main problem concerning LiBH_4 is the chemical stability of the compound. Elevated temperatures of around 600-700 K are needed to cause hydrogen desorption. Thus considerable effort has been put into the reducing of the desorption temperature. Successful destabilization of LiBH_4 has been reported by using catalytic additives [2,3]. While the energetics and electronic structure of LiBH_4 [4,5] has previously been studied using first principles calculations, experimental studies concerning the valence electron structure of LiBH_4 are scarce.

We have studied the electronic structure of LiBH_4 using momentum transfer dependent x-ray Raman scattering (XRS). The momentum transfer dependence of the XRS spectra are used to extract the angular momentum projected density of states.

The experiment was performed using the 9-element analyzer crystal array employing Si (660) reflections in a backscattering geometry. A total energy resolution of 0.75 eV was obtained at the incident energy of 9.69 keV via the use of an additional Si (440) channel-cut monochromator. The Boron K-edge XRS spectra were recorded at two momentum transfer values of 1.7 \AA^{-1} and 9.1 \AA^{-1} . In addition to the B K-edge spectra also the Li K-edge spectra were measured using the abovementioned momentum transfer values.

A commercial grade LiBH_4 powder was used as the sample. Due to the hygroscopic nature of this substance the powder was enclosed in sealed quartz capillaries having a diameter of 2 mm. We encountered some difficulties originating from the coarse granularity of the powder. In order to irradiate a substantial number of granules the sample was wiggled back and forth during the acquisition of the spectra. This however resulted in undulations in the measured spectral intensities. This problem was finally solved via using a defocussed beam having a cross section of $1.5 \text{ mm} \times 2 \text{ mm}$.

While the signal from each analyzer crystal corresponds to a different value of momentum transfer our theoretical calculations indicate, that the momentum transfer dependence of the spectra over the range sampled by the crystals of the multielement array is very slight. The spectra collected from several analyzer crystals can thus be added together resulting in a very good statistical accuracy.

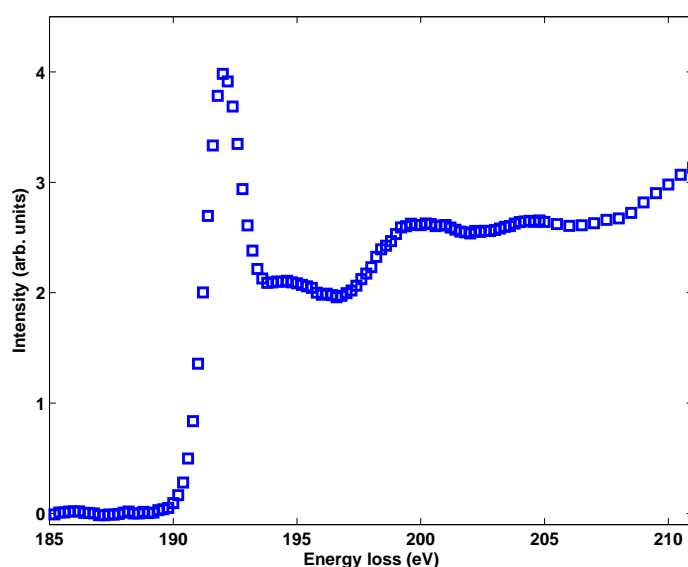


Figure 1: The Boron K-edge of LiBH_4 at the momentum transfer value of 9.1 \AA^{-1} .

- [1] J. K. Kang, S. Y. Kim, Y. S. Han, R. P. Muller, W. A. Goddard III, *A candidate LiBH_4 for hydrogen storage: Crystal structures and reaction mechanisms of intermediate phases*, Appl. Phys. Lett. **87**, 111904 (2005).
- [2] J. J. Vajo, S. L. Skeith, F. Mertens, *Reversible Storage of Hydrogen in Destabilized LiBH_4* , J. Phys. Chem. B **109**, 3719 (2005).
- [3] A. Züttel, S. Rentsch, P. Fischer, P. Wenger, P. Sudan, Ph. Mauron, Ch. Emmenegger, *Hydrogen storage properties of LiBH_4* , J. Alloys Comp. **356-357**, 515 (2003).
- [4] K. Miwa, N. Ohba, S. Towata, Y. Nakamori, S. Orimo, *First-principles study on lithium borohydride LiBH_4* , Phys. Rev. B **69**, 245120 (2004).
- [5] Q. Ge, *Structure and Energetics of LiBH_4 and Its Surfaces: A First-Principles Study*, J. Phys. Chem. A **108**, 8682 (2004).