Synchrotron-based experimental study and theoretical simulation of hydrogen desorption for solid-state hydrogen storage material Mn(BH$_4$)$_2$
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1. Motivation

The main requirements:

- Gravimetric and volumetric density of H: +
- Temperature of desorption: ++++
- Cycling ability: -

Compact and inorganic structure of Mn(BH₄)₂ hydrogen!

Hydrogen fuel cell + solid-state hydrogen storage → breakthrough in mobile applications

Reaction on the anode (dissociation of hydrogen molecules): $H_2 = 2e^- + 2H^+$

Reaction on the cathode (formation of water molecules): $4H^+ + 4e^- + O_2 = 2H_2O$
2. Purpose of study

General aim – determination of thermal decomposition path.

Mn(BH₄)_2 + H₂

T₀ = 120°C

solutions

complementary methods:

- XRPD (X-ray powder diffraction)
- Amorphization process!!!
- XANES (X-ray absorption)
- DFT-modeling and structure prediction (VASP, USPEX – calculations)
3. XAS spectroscopy

XAS  X-ray Absorption Spectroscopy

XANES  X-ray Absorption Near Edge Structure

EXAFS  Extended X-ray Absorption Fine Structure

Electronic structure

Single and multiple scattering description depends on the energy of photoelectron
4. XAS spectroscopy

Some words about physical background

The probability of the electronic transition is determined by density of final states of the system. “Golden Fermi’s rule”

\[
W_{i \rightarrow f} = \frac{2\pi}{\hbar} \left| \langle f \mid H' \mid i \rangle \right|^2 \rho,
\]

Density of final state provides information about local atomic and electronic structures, chemical bonding, optical properties and so on.

What information can be extracted?

- XANES
- EXAFS

Oxidation state of absorbing atoms (Chemical shifts)
5. Experimental details

The scheme of the experiment.

1 - sample holder, 2 - heater, 3 - pressure monitoring system, 4 - hydrogen gas, 5 - X-ray beam, 6 - ionization chamber, 7 - XAS fluorescent detector, 8 XRD detector

The scheme of the experiment.
6. Experimental data

X-ray powder diffraction patterns were obtained at different temperature of the sample. Upon heating the significant broadening of diffraction peaks were observed. This tendency corresponds to amorphization of initial material under heating.

Similar behavior of powder diffraction data for pressure-depends measurements for isomorphic Mg(BH$_4$)$_2$ was described by Y. Filinchuk et., al.

7. Experimental data

Evolution of XANES Mn K-edge spectra of Mn(BH₄)₂ under heating.

Mn K-edge; XANES

Exp. at 30 °C (before desorption)

Exp. at 140 °C (after desorption)

\[ \Delta E = 71.7 \text{ eV} \]

\[ \Delta E = 46.7 \text{ eV} \]

Natoli’s rule predicts a decrease of interatomic distance after heating the sample, \( (E_1 - E_2)R = \text{const} \).

Mn K-edge spectra of Mn(BH₄)₂ have also undergone significant changes upon heating the sample.

TGA analysis.

Drastic weight reduction of Mn(BH₄)₂ observed by Cerny et. al. by the mean of TGA analysis. Up to 9.5% of mass loss were observed at the temperature range from 120 to 160 °C that correspond to the desorption of all hydrogen atoms from the lattice.

We have observed a temperature induced phase transition in Mn(BH₄)₂ which is accompanied by abundant hydrogen release process as well as sample amorphization upon heating!
8. XANES analysis

The stoichiometry of initial material corresponds to formation of manganese diboride as a possible decomposition reaction product:

\[ \text{Mn(BH}_4\text{)}_2 \rightarrow \text{Mn(BH}_4\text{)}_2 \rightarrow \text{MnB}_2 + \text{H}_2 \rightarrow \text{Mn}_x\text{B}_y + \text{H}_2 \]

Various manganese borides should be taken into account. The spectra calculated for Mn\textsubscript{2}B, MnB and MnB\textsubscript{4} in a good agreement with experimental curve of initial material after heating up to 140 °C.

The interatomic distance Mn-B and Mn-Mn of these borides belong to the range 2,17 - 2,21 Å and 2,46 - 2,95 Å respectively compared to 2,44 Å and 4,80 Å obtained by XRD data for initial material.
9. XANES: Fitting

The most probable decomposition paths obtained from the result of formation enthalpy and Gibbs energy DFT-based calculations* assume a formation of Mn metallic phase as a possible decomposition product:

<table>
<thead>
<tr>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Mn(BH}_4\text{)}_2 \rightarrow \text{Mn} + 2\text{B} + 4\text{H}_2$</td>
</tr>
<tr>
<td>$\text{Mn(BH}_4\text{)}_2 \rightarrow \text{MnH}_2 + 2\text{B} + 3\text{H}_2$</td>
</tr>
<tr>
<td>$\text{Mn(BH}_4\text{)}_2 \rightarrow \text{MnB}_2 + 4\text{H}_2$</td>
</tr>
<tr>
<td>$\text{Mn(BH}_4\text{)}_2 \rightarrow \text{MnH}_2 + \text{B}_2\text{H}_6$</td>
</tr>
<tr>
<td>$\text{Mn(BH}_4\text{)}_2 \rightarrow \text{Mn} + \text{B}_2\text{H}_6 + \text{H}_2$</td>
</tr>
</tbody>
</table>

A fitting of linear superposition of Mn K-edge XANES spectra for $\text{Mn}_x\text{B}_y + \text{Mn}_{\text{met}}$ was performed by means of FitIt package**.

The results of fitting reveal that concentration of metallic Mn phase as a possible decomposition reaction products does not exceed 30 ±5%.


10. VASP: DFT modeling

The result of atomic and lattice relaxation: DFT-based modeling (VASP 5.3)

**Model 1:**
Totally occupied hydrogen sites

**Model 2:**
50% of occupied hydrogen sites

**Model 3:**
Totally unoccupied hydrogen sites

Before optimization

After optimization
11. XANES analysis

An accuracy of geometry optimization is approved by XANES Mn K-edge spectra calculated for relaxed structural models. Both a difference in the energy localization and ratio of intensity of “white line” for experimental spectra obtained at 30 °C and 140 °C are accurately reproduced at the calculated XANES spectra for models with totally occupied and totally unoccupied hydrogen positions (model 1 and model 3).

The associative between energy localization of absorption peaks (A -> B, A* -> B*) suggests that interatomic distance Mn-B = 2.17 ± 0.05 Å and Mn-Mn = 2.72 ± 0.18 Å have determined correctly.
12. USPEX: Evolutionary algorithm

USPEX – Universal Structure Predictor Evolutionary “Xtallography”
Cycle of global minimum searching for multidimensional energy landscape.

Evolutionary algorithm based on generation of numerous structural models and further selection of the more stable low-energy structures. The revolution idea is AB-initio local optimization and free energy calculation for relaxed structures for each structural models which can be generated randomly, by heredity or lattice mutation and so on.

The most stable structural models obtained by USPEX for dense Mn-B system. Structural model obtained by energy minimization with a different amount of hydrogen in the red box. The structures with the lower value of free energy obtained by USPEX are in the green box.
Table of structural parameters for the most probable structural models obtained by energy minimization (VASP 5.3 code) and evolutionary algorithm (USPEX code).

<table>
<thead>
<tr>
<th>Lattice parameters</th>
<th>VASP model Mn₉B₁₈</th>
<th>USPEX model Mn₉B₁₈</th>
<th>USPEX model Mn₉B₁₈</th>
<th>USPEX model Mn₈B₁₆</th>
<th>USPEX model Mn₈B₁₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>̅a (Å)</td>
<td>5.7853</td>
<td>5.1380</td>
<td>7.5461</td>
<td>5.1523</td>
<td>4.7065</td>
</tr>
<tr>
<td>̅b (Å)</td>
<td>7.5754</td>
<td>6.4529</td>
<td>7.1143</td>
<td>6.4508</td>
<td>5.2770</td>
</tr>
<tr>
<td>̅c (Å)</td>
<td>7.5286</td>
<td>6.9740</td>
<td>3.8731</td>
<td>6.9594</td>
<td>7.0625</td>
</tr>
<tr>
<td>α</td>
<td>98.0845</td>
<td>101.2459</td>
<td>92.7232</td>
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<td>γ</td>
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<td>86.5546</td>
<td>108.6317</td>
<td>90.0003</td>
</tr>
<tr>
<td>V_{unit cell} (Å³)</td>
<td>216.28</td>
<td>206.36</td>
<td>206.06</td>
<td>206.3361</td>
<td>175.41</td>
</tr>
<tr>
<td>Группа симметрии</td>
<td>P 1</td>
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<td>C 2/m 2/c</td>
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</tr>
<tr>
<td>Плотность (г/см³)</td>
<td>5.290</td>
<td>5.545</td>
<td>5.553</td>
<td>5.545</td>
<td>5.798</td>
</tr>
</tbody>
</table>

\(-7,776\)
XANES simulations for the structures predicted by evolutionary algorithm show that the best agreement with experimental curve at T=140 °C were obtained for models without space symmetry group, while the structures with sharp RDF peaks at the 1st and 2nd coordination spheres are not coincide with experimental XANES curve.

<table>
<thead>
<tr>
<th>Model</th>
<th>Mn-B distance (Å)</th>
<th>Mn-Mn distance (Å)</th>
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<td>XRD. Mn(BH4)2 before heating</td>
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14. Conclusions

1) **X-ray powder diffraction** in combination with **TGA analysis** indicate that process of material amorphization under heating is accompanied by abundant hydrogen release. XANES spectra also undergo significant changes upon heating the sample.

2) **XANES** analysis in combination with AB-initio DFT-based structural modelling represent an powerful equipment of the local atomic structure investigation for the nanoscale and amorphous materials.

3) The result of **geometry optimization** reveals collapse of porous structure as well as amorphization process after the hydrogen atoms were partially or totally removed from the structure.

4) Significant decrease of **Mn-B** and especially **Mn-Mn** interatomic distances were obtained from AB-initio DFT modelling upon hydrogen release. It is a good confirmation of Natoli’s rule prediction.

5) It was assumed that the sample after heating has **unhomogeneous structure** with a **nanodomain features** corresponding to various crystalline atomic ordering.

6) Several low-energy structural models were obtained by the mean of **evolutionary algorithm** implemented in **USPEX code**.

7) **XANES spectra** calculated for the relaxed structures in a good agreement with experimental data. This fact is approve a correctness of the result of geometry optimization.
THANK YOU FOR ATTENTION!!!
13. USPEX: structure predictions

An accuracy of modeling is approved by XANES Mn K-edge spectra calculated for structural models predicted by the mean of Evaluationary algorithm which is implemented in USPEX code. The XANES spectra simulated for the more stable low-energy structures in a good agreement with the experimental curve obtained after heating the sample. Such a way we can conclude that interatomic distance and structural changes were determined correctly.

Results of DFT-based modeling in comparison with the XRD.

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The most probable structural models for Mn-B systems predicted by means of USPEX algorithm:

1. 
2. 
3. 
4. 
5. 
6. 
7.

Different kinds of variations operators

The supercell 2x2x2 for predicted structure of Mn-B system
Моделирование рентгеновских порошковых диффрактограмм XRPD

Расчетная формула для оптимизации ширины дифракционных пиков с целью учета их уширения в результате аморфизации исходного материала:

\[
\text{Int}(\theta, \gamma) = \sum_{k=0}^{n} C \frac{I_k \cdot \gamma}{(\theta - \theta^k_o)^2 + \gamma^2}
\]

Где:
- \(I_k\) — значение интенсивности \(k\)-го пика;
- \(\theta^k_o\) — угловая локализация \(k\)-го пика;
- \(C\) — нормировочная постоянная;
- \(\gamma\) — варьируемый параметр.
На следующем этапе была проведена оценка адекватности применяемой методики расчета. Также были смоделированы XRD спектры для возможных продуктов реакции разложения с учетом уширения дифракционных пиков.

Теоретически рассчитанный XRD спектр для борогидрида марганца MnB₂H₈ в сравнение с экспериментальной кривой до десорбции водорода

Теоретическое моделирование XRD спектров для возможных продуктов реакции разложения исходного соединения MnB₂H₈
A, B, C - суперпозиция XRD спектров с весовыми коэффициентами полученными в результате фитинга спектров поглощения

D, E, F – суперпозиция XRD спектров с весовыми коэффициентами, полученными в результате фитинга рентгеновских дифрактограмм с учетом уширения пиков
Формула Шеррера позволяет оценить размер области когерентности по ширине дифракционных максимумов:

$$L = \frac{k\lambda}{\beta \cos \vartheta}$$

- $k$ — форм фактор;
- $\lambda$ — длина волны;
- $\beta$ (FWHM) — полная ширина на половине максимума;
- $\vartheta$ — угловая локализация максимум