Experimental report

31/01/2022

Proposal:	**5-24-657**	**Council:**	4/2020
Title:	In-situ study of hydrogenation dynamics and structure development in LaFeSiD_x using thermograviometry and neutron diffraction.		
Research area:	Physics		

This proposal is a new proposal

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Samples:	LaFeSiD LaFeSi LaFeSiO

Instrument	Requested days	Allocated days	From	To
D1B	3	2	01/03/2021	03/03/2021

Abstract:

With the recent discovery of the novel iron-based superconductor LaFeSiH it is of great interest to understand how the physical properties and the structure changes with different levels of H in the range 0<x(H)<1. We propose to probe the structure of the compound in-situ using neutron diffraction coupled with thermogravitometry during the absorption and desorption of H (D will substitute H in the experiment). This experiment will allow us to understand the intermediate structure between the fully hydrogenated and de-hydrogenated compound (which is not superconducting). By understanding the structural changes in the compound and linking it to subsequent physical properties measurements we can gain a further insight to the underlying physics of this iron-based superconductor. The mechanisms behind iron-based superconductivity is still debated to this day and the outcome of this experiment will serve as a piece of the puzzle in understanding these mechanisms.

In-situ deuteration of LaFeSi using Neutron diffraction

(Dated: January 31, 2022)

A. Heating LaFeSi under vacuum

The precursor was heated to 180 °C under vacuum and the structure was followed in-situ. A temporal resolution of 1 min was used up to 400K where it was changed to 3 min in order to improve counting statistics. Sequential Le bail refinements were carried out to follow the unit cell parameters as a function of the temperature. The unit cell parameters determined from the refinements are shown in figure 1 and 2.

The precision is clearly not very high due to the short counting time of the measurements, however, combining several measurements will lead to a deterioration of the temporal resolution and thus increase the error of the temperature. It is clear from the data that the c-axis increases with temperature while the increase of the a-axis is on the border of detection with the experimental conditions chosen here. The expansion of the unit cell is as expected upon heating and is not the center of this study.

B. Deuteration of LaFeSi

The temperature was stabilized at 180 °C and Deuterium gas was introduced into the sample chamber. The first NPD acquisition and initiation of the first gas injection cycle were synchronized such that the gas pressure in the chamber and the recorded patterns can be correlated. In figures 3 and 4 the NPD patterns are plotted as a function of time. Two cuts in 2 theta have been chosen here to avoid contributions from the sample environment, making visual inspection easier since the signal from the sample environment is very high.

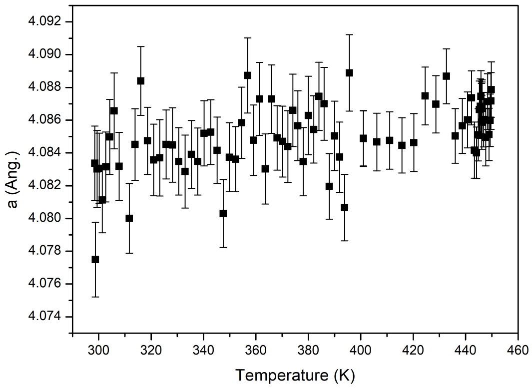

FIG. 1. The *a* unit cell parameter of LaFeSi as a function of temperature, during heating.

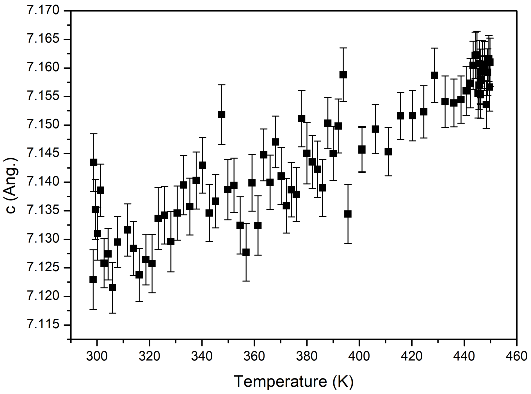

FIG. 2. The *c* unit cell parameter of LaFeSi as a function of temperature, during heating.

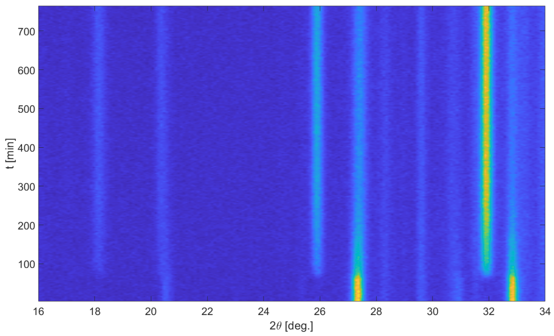

FIG. 3. Time resolved NPD patterns showing the transition from LaFeSi to LaFeSiD at low 2 theta values.

From the two figures we clearly see a strong decrease in the contributions from the LaFeSi phase and the emergence of a new phase, which can be indexed as LaFeSiD. This transition happens around 1 hour after the first injection. This delay in the reaction is due to the incubation time of the reaction, this is common place for hydrogenation reactions and has been observed in several occasions for this compound. The shape and unit cell parameters of LaFeSi, LaFeSiD and LaFe2Si2 were refined using the patterns collected before and after the deuteration and these parameters were used in a sequential Rietveld refinement which varies only the scale factor. From this the volume fraction of the three phases can be calculated. In figure 5 the calculation is shown as a function of time. In the same plot the Deuterium uptake in the sample is plotted as a function of time and the correlation between the uptake and the formation of the LaFeSiD phase is very clear.

From the Deuterium uptake one can also calculate the

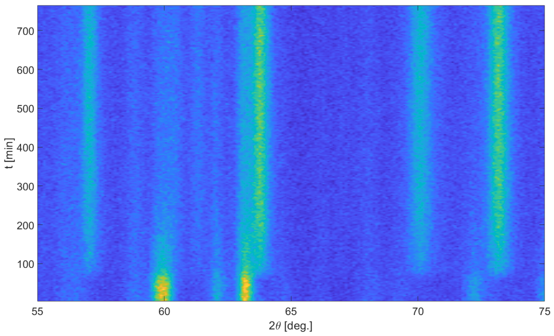

FIG. 4. Time resolved NPD patterns showing the transition from LaFeSi to LaFeSiD at large 2 theta values.

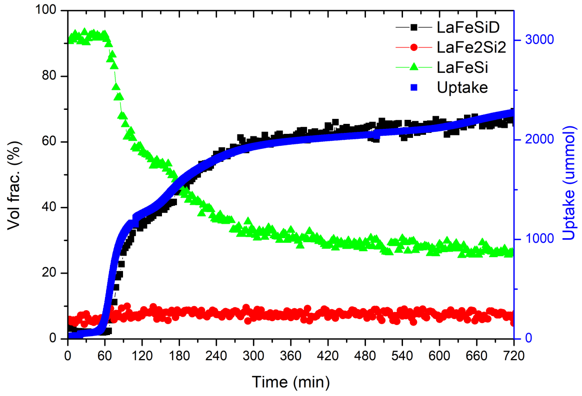

FIG. 5. Volume fraction of phases as determined by NPD plotted with the calculated deuterium uptake.

expected volume fraction of LaFeSiD in the sample as a function of time. In figure 6 this calculation is shown and compared with the values obtained from the Rietveld refinements. The two values are in good agreement although there are small discrepancies in the values.

Inspecting the evolution of the volume fraction further it is clear that there are features in the uptake, most notably at the two hour mark. This can be explained by the injection cycles which were performed during the experiment. In figure 7 The correlation between the structure in the uptake graph and the injections can be seen clearly.

The temperature of the sample was also monitored during the experiment. This data is also interesting to consider since it provides, though qualitative, information about the thermodynamics of the deuteration reaction. In figure 8 the temperature of the sample is plotted as a function of time and a very clear peak can be seen, starting just after the 1 hour mark, coinciding with the beginning of the absorption.

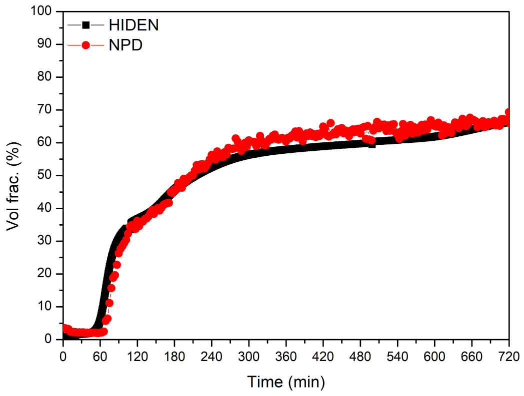

FIG. 6. Volume fraction of LaFeSiD as determined by NPD and from the Deuterium uptake.

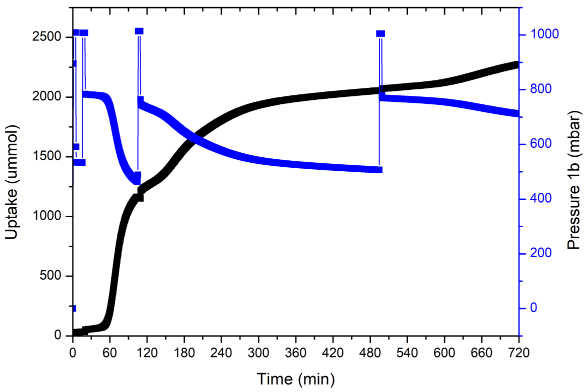

FIG. 7. The uptake of deuterium ploted with the deuterium injection curves

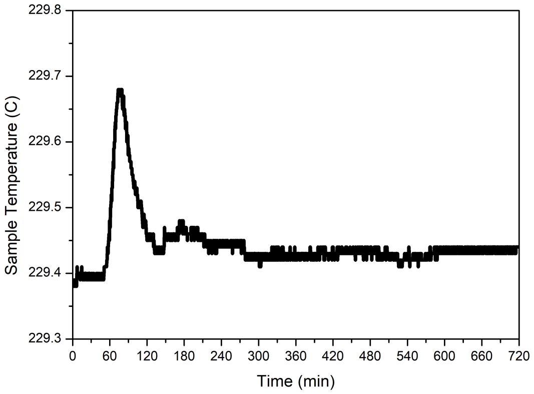

FIG. 8. The temperature of the sample as a function of time. A peak is seen at the start of the reaction indicating an exothermic behaviour.

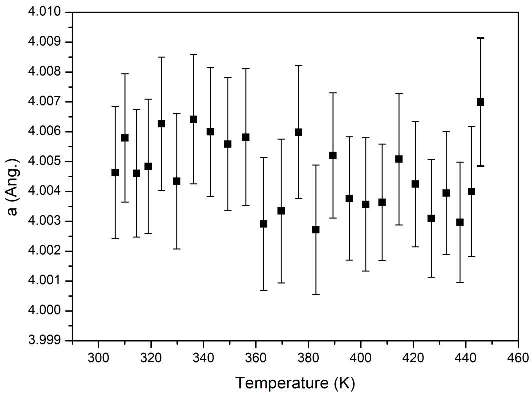

FIG. 9. The *a* unit cell parameter of LaFeSi as a function of temperature, during cooling.

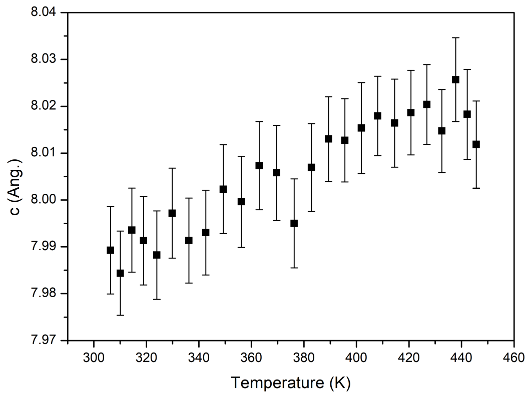

FIG. 10. The *c* unit cell parameter of LaFeSi as a function of temperature, during cooling.

C. Cooling LaFeSiD in Deuterium

After the deuteration reaction the sample was cooled to room temperature again. During this cooling NPD patterns were collected and in the same fashion as the heating of the sample the unit cell parameters were followed using sequential le bail refinements. In figures 9 and 10 the unit cell parameters of LaFeSiD are plotted as a function of temperature. The same trend is observed here as was observed during the heating of LaFeSi.

I. CONCLUSIONS

It can be concluded from the NPD experiment that the hydrogenation of LaFeSi is a binary reaction with an equilibrium between two phases following the reaction below:

$$LaFeSi(s) + H_2(g) \rightleftharpoons 2LaFeSiH(s)$$

The kinetics are somewhat inconclusive due to restraints in available pressure/volume of the experimental setup that necessitated injections during the experiment. This is problematic for fitting the kinetics with different models to investigate what acts as the rate determining step in the absorption process.