（ ※本報告書は英語で記述してください。ただし、産業利用課題として採択されている方は日本語で記述していただいても結構です。）

J-PARC MLF Experimental Report	提出日 Date of Report
課題番号 Project No. 2012B0081 実験課題名 Title of experiment Anomalous lattice vibrational modes in lithium alanates, – Towards hydrogen release mechanism in hydrogen storage – 実験責任者名 Name of principal investigator Keisuke Tomiyasu 所属 Affiliation Tohoku University	装置責任者 Name of responsible person Kenji Nakajima 装置名 Name of Instrument/(BL No.) AMATERAS (BL14) 実施日 Date of Experiment from noon, 19 January, 2013 to night on 25 January, 2013, including half-day run on 23 Jan. (total 6 days)

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）

Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

$LiAlD_4$, powder

2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）
Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

I. INTRODUCTION

Efficient hydrogen storage is a critical feature of the hydrogen economy. The most attractive candidate/prototype materials for this purpose have been the aluminum complex hydrides (so-called alanates). The general reaction is described by

$$3MAlH_4 \leftrightarrow M_3AlH_6 + 2Al + 3H_2\,(g) \leftrightarrow 3MH + 3Al + 9/2H_2\,(g), \qquad (1)$$

where M^+ denotes the alkali metal cations Na^+ and Li^+. The alanates $MAlH_4$ and M_3AlH_6 comprise M^+ cations and Al hydrido complex anions, $[AlH_4]^-$ and $[AlH_6]^{3-}$, respectively.

Many researchers have so far attempted to identify the microscopic mechanism behind the decomposition reaction. Among these, very recently, using the triple-axis spectrometer TOPAN, we have investigated pDOS energy (E) spectra of lattice vibrations from 20 K to room temperature in $LiAlH_4$, which decompose to release hydrogen over 423 K. As the result, we found that the hydrogen release originates rather in bulk low-energy

2. 実験方法及び結果（つづき） Experimental method and results (continued)

librational modes of the $[AlH_4]^-$ complexes, occurring at surprisingly low temperature of ~100 K, than in the high-energy hydrogen bending and stretching modes near decomposition temperatures that have been mainly paid attention so far.

Here, we further investigate the anomaly with respect to both energy (E) and momentum (Q) using $LiAlD_4$.

II. EXPERIMENTS

A high-resolution chopper spectrometer, AMATERAS, was used. The multi-E_i values were 10, 23, and 94 meV. The sample was shaped in the very thin cylindrical form. The standard closed-cycle refrigerator and special thin Al cell were used.

III. RESULTS

Figure shows the temperature dependence of $S(Q,E)$, measured at E_i = 94 meV. At the lowest temperature, the clear phonon signals are observed. The intensity scale is reduced with increasing the temperature, which is most probably due to the sum rule and the detailed balance law. (1) As the temperature increases, however, the patterns are significantly smeared towards 300 K in the E direction, whereas this is not the case rather in the Q direction. This fact suggests that the phonons are unstable in terms of time but the spatial polarization type is rather sustained even at 300 K. (2) Further, as shown by the dotted line defined by the energy of peak top at ~3 Å^{-1}, the peak position of same phonon appreciably shifts to the higher-energy side in the high-Q region above ~5 Å^{-1}. This behavior suggests the existence of another scattering in the lower energy region, probably quasielastic scattering of librational/rotational motions of the $[AlH_4]^-$ complexes. Thus, it is considered that $LiAlH_4$/$LiAlD_4$ exhibit disorder in the orientation of complexes like in so-called plastic crystal. Further analyses are under investigation.

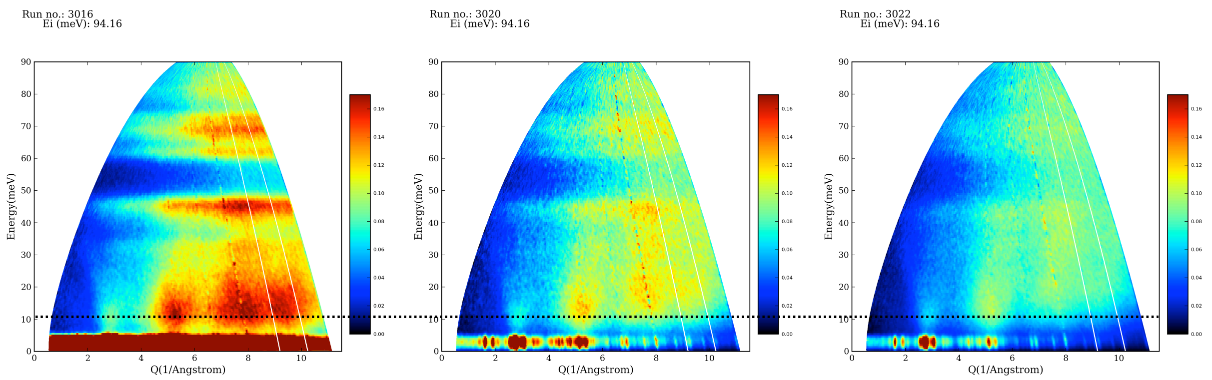

Figure: Inelastic neutron scattering intensity distribution in Q and E space, $S(Q,E)$, measured at 7, 200, and 300 K. For comparison, the Bose population factor was corrected. The intensity scale was unified among the three panels. The dotted line is guide for eye.