Origin of the large anharmonicity in the phonon modes of LiBH$_4$

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ABSTRACT

The dynamics and bonding of the complex hydride LiBH$_4$ have been investigated by vibrational spectroscopy and density functional theory (DFT). The combination of infrared, Raman, and inelastic neutron-scattering (INS) spectroscopies on hydrided and deuterated samples reveals a complete picture of the dynamics of the BH$_4^-$ ions as well as of the lattice. Particular emphasis is laid on a comparison between experiment and theory, revealing significant discrepancy between the two approaches for vibrations with high anharmonicity, which is related to large vibrational amplitudes. The latter is typical for librational modes in molecular crystals and pseudo-ionic crystals such as complex hydrides. The presented strategy for anharmonic frequency corrections might thus be generally applicable for this kind of materials.

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1. Introduction

Complex metal-hydrides [1,2] show a dual nature: Similar to molecular solids, they contain pseudo-ions, such as BH$_4^-$ in LiBH$_4$ built by strong covalent bonds between B (Al, Ga,...) and hydrogen. In addition, these charged units form ionic salts together with counter ions such as Li$^+$ ions. This duality is revealed at best by vibrational spectroscopy, where lattice (so-called external) vibrations coexist with internal vibrations of the BH$_4^-$ pseudo-molecule. The latter encompass stretching and bending of the B–H bonds and are observed at high energies, well-separated from the lattice modes. The qualitative understanding allows for a straightforward interpretation of isotope effects, used in, e.g., hydrogen–deuterium labeling on LiBH$_4$ for the measurement of BH$_4^-$ stretching modes anharmonicities [3] and the determination of hydrogen diffusion mechanisms in borohydrides [4–6]. Interestingly, though, is the fact that despite the rather simple interpretation, density-functional theory, which is based on harmonic approximation of the phonons, overestimates the energy of the stretching modes by 50 to 80 cm^{-1} (6–10 meV) [4,7]. Furthermore, the difference depends on the specific mode and thus mode assignment by simple comparison of theory and experiment is error-prone.

The presence of pseudo-ions within the lattice also affects the lattice phonon modes, with the appearance of constrained rotations (librations) modes at energies right above the band of optical vibrations [8]. The very existence of the librational modes depends on the connection of the pseudo-ion to the lattice. In LiBH$_4$, the energetically highest translational motions have relatively high energy due to the small mass of the Li atom [9]. Furthermore, reorientation of the molecule (quasi-free rotation) occurs as well, if the corresponding energy barriers are low enough [10,11]. These motions with an energy of only a few meV can couple to the more energetic lattice modes or to librational modes, as shown for analogous molecular crystals [12,13].

The term 'coupling' requires additional explanation. The description of motions in a crystal by 'librational' and 'translational' modes and a coupling of them is purely depictive. The motions correspond to the normal vibrations resulting from the energy potential respectively symmetry of the crystal. However, they are well approximated by 'librational' and 'translational' modes not representing the exact motion of the atoms. The discrepancy from the simplified motion may be described as a mixing between the extreme cases. Apart from a simplified description, the idea of a coupling can be used to explain the special behavior of these motions, e.g. large frequency shifts as function of temperature of certain lattice modes [7,9]. These shifts can be only partly explained by volume driven anharmonicity, and a large part of it has been attributed to the intrinsic anharmonicity of the librational modes [9,14]. Both anharmonicity and dynamic disorder of the BH$_4^-$ group will in turn affect structural and therefore physical properties of LiBH$_4$ [15].

In this work, we study external modes in LiBH$_4$ and LiBD$_4$ by INS measurements and *ab initio* methods. We first present simulated INS spectra, phonon density of states (PDOS) and band structures of the complex hydride. The vibrational frequencies at the Brillouin zone center and the corresponding infrared and *Raman* intensities are discussed in conjunction with previous vibrational studies [16,17,7,9].

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In a synergetic approach between experiment and theory, we then find the existence of mixed librational-translational modes. These modes, together with the conventional librational modes, present a high anharmonic character due to their hydrogen-dominated, large amplitudes-of-motion. This is evidenced by the large calculated anharmonic correction on their vibrational frequencies and their high sensitivity to H/D partial isotopic substitution.

The exact calculation of vibrational amplitudes requires electronic structure calculations as utilized here. However, the value may be estimated by considering the character and mass of atoms involved in the specific vibrational mode. We discuss how this can be used to assess the agreement between experimental and calculated vibrational spectra in complex hydrides in general.

2. Experimental methods

2.1. Materials preparation

LiBH$_4$ is purchased from SigmaAldrich Fine Chemicals, Switzerland, (95%), and LiBD$_4$ from Katchem, Czech Republic (98%). The samples are handled solely in argon glove boxes for preparation and measured without contact to air. Hydrogen–deuterium exchange in LiBH$_4$ is monitored by the mass change in a magnetic suspension balance Rubotherm (Bochum, Germany). Three partially exchanged LiBH$_{4(1-x)}$D$_{4x}$ samples (1g) of nominal compositions $x = 0.23, 0.48$ and 0.76 were obtained by exposing LiBH$_4$ to a $2 \cdot 10^6$ Pa D$_2$ gas pressure at 538 K for various time intervals (up to 36 h for $x = 0.90$). FTIR measurements were performed in transmission on thick films deposited on 2 mm CaF$_2$ substrates. For making films, the bulk samples were first diluted in tetrahydrofuran (THF). The filtered saturated solutions were then deposited on 2 mm thick CaF$_2$ windows and dried at 90°C in the argon glove box for 30 min, resulting in 20–60 µm thick films. The CaF$_2$ window was mounted in Ar in a brass cell, with another CaF$_2$ window on top, separated by a 6 mm Teflon spacer.

2.2. Inelastic neutron scattering

INS spectra have been recorded at the TOSCA spectrometer, ISIS. The measurements were carried out in neutron energy loss mode on samples containing only isotope 11 of boron to avoid the high neutron absorption of ^{10}B present in natural boron. The Li^{11}BH$_4$ powder was mounted into a flat aluminum sample holder of 1 mm thickness. The signal of the empty aluminum sample holder and a flat background have been subtracted. The raw data was corrected to obtain the scattering function $S(Q, \omega)$ using standard routines available at ISIS.

2.3. Raman spectroscopy

Raman spectra were obtained in backscattering geometry using a Renishaw Ramascope 2000 (Renishaw plc, Gloucestershire, UK) with a spectral resolution of 1 cm^{-1}. The 633 nm line of the HeNe-laser was focused on the sample through a 20 times magnifying objective of the microscope (beam diameter approximately 20 µm), the laser beam power on the sample being 2.8 mW. The spectrometer was equipped with a CCD camera detector and a 2nd CCD camera to obtain the optical image of the sample, from which the crystal size is determined. Around 20 mg of LiBH$_4$/LiBD$_4$ were placed in a Linkam THMS600 cell (Linkam Scientific Instruments, UK) directly adapted to the microscope of the instrument; the cell allows the use of controlled atmosphere and temperature. The glass window of the cell is 0.1 mm thick. The sample is kept in a flow of 100 cm^3/min deuterium and hydrogen flow, respectively, up to the final temperature. Additional low temperature Raman

spectra have been taken from literature [18,19] taken with a commercial micro- Raman spectrometer (Jobin Yvon LabRam HR), adapted to the cryostat. The excitation radiation was the 532 nm wavelength line of a diode-pumped Nd:YAG laser of 50 mW.

2.4. FTIR spectroscopy

All measurements were performed in transmission at 298 K with a Bio-Rad 175C FTIR spectrometer in nitrogen atmosphere.

2.5. Ab initio calculations

The normal mode vibrational analysis of LiBH$_4$ and LiBD$_4$ was performed with *ab initio* lattice dynamics based on density-functional theory and the plane-wave pseudopotential method as implemented in the CASTEP code [20,21]. Pseudopotentials were of the optimized norm-conserving variety [22] with a plane-wave cutoff of 450 eV. Calculations were performed under the PBE approximation to exchange and correlation [23]. Brillouin-Zone integration was performed according to the Monkhorst–Pack scheme with a $2 \times 3 \times 2$ mesh of k-points, which gave convergence of all modes to a precision of better than 3 cm^{-1}. Pseudopotential errors in the frequencies were estimated at no more than 1% from a comparison of alternative pseudopotentials. The normal modes of the crystalline phase were determined from dynamical matrices calculated using density-functional perturbation theory (DFPT) [24,21].

The INS spectra were generated using the aClimax program [25]. Anharmonic frequency corrections were derived from the cubic and quartic expansion coefficients of the potential energy surface.

3. Experimental results

LiBH$_4$ is orthorhombic (*Pnma*) under normal conditions and undergoes a first-order phase transition upon heating at 381 K to a hexagonal high-temperature phase (*P6$_3$mc*) [26]. The results are organized as follows: after an overview of all vibrational spectra, the INS spectra are compared to the *ab initio* harmonic calculations and the multiphonon contribution extracted/separated. The one phonon contributions are then put in correspondence with the calculated densities of states and band structures. Subsequently, we present a detailed analysis of the INS external modes, as a function of H/D exchange and temperature, focussing on anharmonicity of the translational-librational modes. We do not discuss the internal modes: extensive Raman [19,9,4] and infrared [16,3,27] studies already exist on the subject. (see Table 1).

3.1. Vibrational properties of LiBH$_4$ and LiBD$_4$

Inelastic neutron spectroscopy (INS) spectrum is the amplitude-of-motion and neutron incoherent cross section weighted phonon density of state [8]. It is hence ideally suited for the observation of external modes in LiBH$_4$ due to the large hydrogen amplitudes-of-motion and cross section. While Raman and infrared observable

Table 1
Relaxed structural parameters used for the calculation of the vibrational properties of LiBH$_4$ and LiBD$_4$ in the low-T phase. Space group *Pnma* (No. 62). $a = 7.179$ Å, $b = 4.437$ Å, $c = 6.803$ Å.

Site	x/a	y/b	z/c
Li/4c	0.15802	0.25	0.10776
B/4c	0.31058	0.25	0.42663
H1/4c	0.91353	0.25	0.93066
H2/4c	0.4019	0.25	0.27446
H3/8d	0.2098	0.02876	0.42884