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Low-lying phonons in $NaBH_4$ studied by inelastic scattering of synchrotron radiation

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Acoustic phonon dispersion has been measured in the cubic phase of $NaBH_4$ by the inelastic x-ray scattering (IXS) technique using single crystals of natural isotope composition at room temperature. Experimental results are compared with the compressibility data and the previously published *ab initio* calculations. Comparison of the elastic properties derived from the diffraction and IXS experiments indicates a non-negligible contribution (below 10%) of nonhydrostatic effects in the diffraction experiments. Strong preferred orientation in the compressed samples is also revealed by Rietveld analysis of the synchrotron powder-diffraction data.

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I. INTRODUCTION

The renewal of the interest to light hydrides is motivated by their ability to store hydrogen. Borohydrides of the light metals are considered to be among the most promising candidates for hydrogen storage.[1] However, storage properties of borohydrides are far from being well understood and optimized thus calling for more efforts from both experimentalists and theoreticians. In particular, despite the large technological relevance of borohydrides,[2] there are only few reports on their elastic properties which are, to the best of our knowledge, limited by the polycrystalline average. The bulk moduli have been estimated from diffraction data for a few polymorphs of $LiBH_4$ (Ref. 3) and $NaBH_4$ (Ref. 4); *ab initio* calculations of the bulk modulus and phonon dispersions are also available.[5,6] Since the elasticity is a function of interatomic interactions, it is of interest for both theory and applications. The lack of sufficiently large single crystals and their chemical instability makes the application of classical experimental techniques, such as ultrasonic measurements or Brillouin light scattering, very difficult.

The most complete information on the lattice dynamics, including the long-wave limit, could be extracted from a single-crystal inelastic-scattering experiment. In the case of light borohydrides the inelastic neutron-scattering (INS) experiment is impaired because of very high incoherent scattering by hydrogen and high absorption of boron. Inelastic x-ray scattering (IXS) overcomes the sample size problem critical for INS and, compared to ultrasonic methods, is not sensitive to the defect structure of the material.

Here we report on the dispersion of acoustic phonons in the single crystal of $NaBH_4$ of natural isotope composition measured by IXS at ambient conditions. Several groups of optical phonons have also been observed in our IXS study. Their dedicated study will be published elsewhere. Long-wave extrapolation provides the elastic moduli which are compared with the bulk modulus extracted from the diffraction data collected as a function of pressure. We deal with experimental determination of acoustic dispersions and application of IXS to study lattice dynamics in a hydrogen storage material.

II. EXPERIMENT

Single crystals of $NaBH_4$ were obtained by slow evaporation of a filtered saturated solution of $NaBH_4$ in isopropylamine under nitrogen flow, varying thus slightly the crystal-growth procedure described earlier.[7] The maximum size of the crystals thus obtained was $3\times3\times3$ mm^3. The crystal used for this study was about $2\times2\times2$ mm^3 with rocking curve for (200), (220), and (222) reflections as narrow as 0.03°.

The IXS experiment was performed on beamline ID28 at the European Synchrotron Radiation Facility. The instrument was operated at 17 794 eV, providing an overall energy resolution of 3.0 meV full width at half maximum (FWHM). Direction and size of the momentum transfer were selected by an appropriate choice of the scattering angle and the sample orientation in the horizontal scattering plane. The momentum resolution was typically set to 0.28 and 0.84 nm^{-1} in the horizontal and vertical planes. Further details of the experimental setup can be found elsewhere.[8] The dimensions of the focused x-ray beam were 250×60 μm^2 (horizontal × vertical FWHM). The experiment was performed in a transmission geometry and at room temperature. The fitting of scattered intensity as a function of momentum transfer has been done with a sum of Lorentzians corresponding to phonon annihilation and creation with relative weights satisfying the detailed balance condition plus Lorentzian elastic line convoluted with the resolution function.[9]

The elastic modules are obtained via the sound velocities v, as derived from the initial slope of the acoustic phonon branches along specific (mostly high-symmetry) directions, either by a linear or by a sinusoidal fit (formally equivalent to limiting the interatomic interactions to nearest neighbors), and Christoffel's equation $|\mathbf{v}^2-\mathbf{\Lambda}|=0$ (Ref. 10) using the expression

$$\Lambda_{jk}=\frac{1}{\rho}C_{ijkl}n_in_l, \tag{1}$$

where $\tilde{C}$ is the elastic tensor, ρ is the crystalline density, and $\mathbf{n}$ is the unit vector collinear with the phase-velocity vector. An iterative correction procedure was implemented; this is

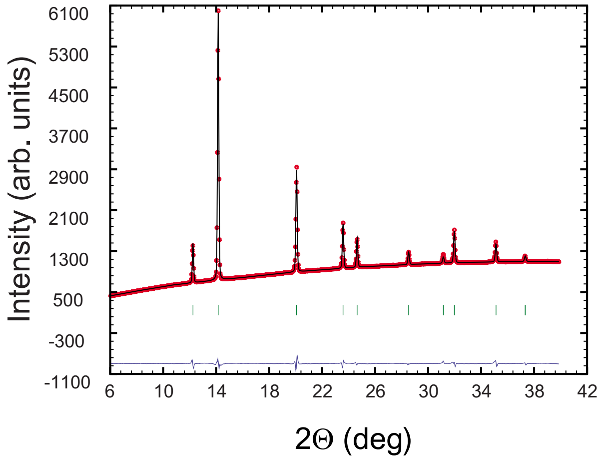

FIG. 1. (Color online) Powder-diffraction pattern collected at $p=3.64$ GPa (dots) together with the calculated and difference curves (lines). Vertical bars indicate positions of Bragg peaks.

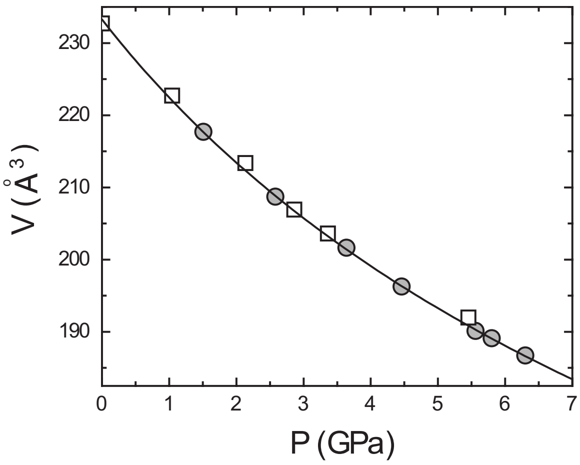

FIG. 2. Unit-cell volume as a function of pressure for the cubic phase of NaBH$_4$. Circles denote data points for this work while squares correspond to the data from Ref. 11.

based on the calculation of correction coefficients linking theoretical phonon energy and simulated result of integration over the opening of analyzer. Those correction coefficients are then applied to the experimental data. In practice, the second iteration already gave negligible corrections.

Diffraction patterns were recorded at the Swiss-Norwegian Beam Lines (SNBL) of ESRF at the wavelength $\lambda=0.7186$ Å using a MAR345 Image Plate detector. The powder sample was loaded into a diamond-anvil cell together with a ruby chip for pressure calibration (more details can be found in Ref. 4). The data were collected at five pressure points below cubic-to-orthorhombic phase transformation[4] ($p=1.51, 2.58, 3.64, 4.46, 5.56, 5.85$ GPa); since this transition is of the first order, one more point from a coexistence region at $p=6.36$ GPa is also included in the analysis. Note that similar to the previously reported studies[4,11] all the measurements have been done at room temperature and no pressure-transmitting medium has been used.

III. RESULTS AND DISCUSSION

We start from the analysis of the powder-diffraction data aiming to get first a rough estimate of the elastic properties. At variance with previously published results where only unit-cell constants were reported,[11] we have done a full profile analysis by the Rietveld method as it is implemented in FULLPROF software.[12] Starting from the cubic Fm-$3m$ structural model[13] we achieved a discrepancy factor $R_{\text{Bragg}}=13.2\%$ and our analysis of the difference curve has shortly uncovered a strong preferred orientation. The patterns were then successfully modeled using the March-Dollase model assuming a plate habit of coherently scattering volumes; $R_{\text{Bragg}}=1.51\%$. As expected, this correction is found to be pressure independent. The texture parameter varies between 0.694(2) and 0.702(2) for five pressure points. The experimental diffraction pattern together with the difference and calculated curves is shown in Fig. 1 for $p=3.64$ GPa.

The unit-cell volume derived from our diffraction experiment is shown in Fig. 2 together with the data taken from the previous publication.[11] Diffraction data can be nicely fitted by the Murnaghan equation of state (EOS) as follows:

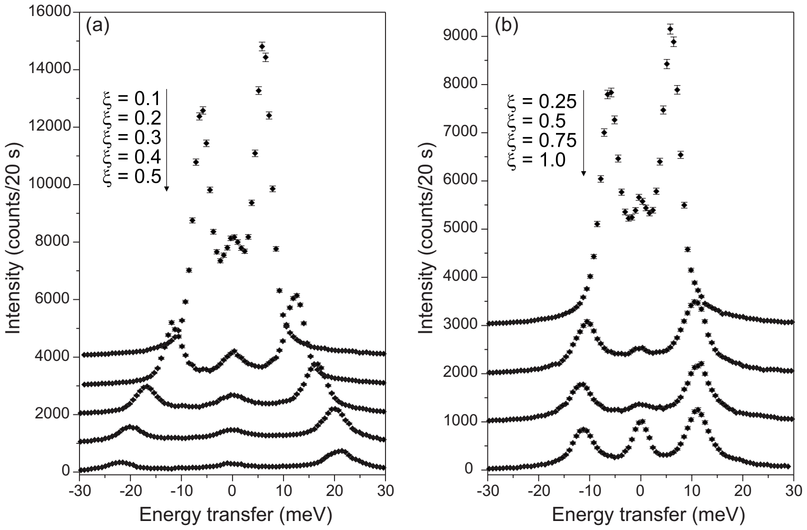

FIG. 3. Selected IXS spectra of NaBH$_4$ at the indicated ξ values (given in reciprocal-lattice vector units) (a) for the LA [111] branch with momentum transfer $[2+\xi\ 2+\xi\ 2+\xi]$ and (b) for the TA $[110]_{\langle 1-10\rangle}$ with momentum transfer $[2+\xi\ 2-\xi\ 0]$. The spectra are shifted along the vertical direction for clarity, conserving the same intensity scale.

TABLE I. Experimental configurations for the measured dispersion branches. Parameter ξ is always positive. Asterisks indicate values used for calculation of the elastic modules.

Notation	Momentum transfer	Propagation	Polarization	Velocity (km/s)
LA [100]	$[2+\xi\ \ 0\ \ 0]$	[100]	$\langle 100\rangle$	4.97(10)*
TA [100]	$[4\ \ \xi\ \ 0]$	[010]	$\langle 100\rangle$	2.90(6)*
LA [111]	$[2+\xi\ \ 2+\xi\ \ 2+\xi]$	[111]	$\langle 111\rangle$	5.37(10)
TA [111]	$[2-\xi\ \ 2+\xi\ \ 2+\xi]$	[111]	$\langle 2-1-1\rangle$	2.55(20)
LA [110]	$[2+\xi\ \ 2+\xi\ \ 0]$	[110]	$\langle 110\rangle$	5.06(10)*
TA $[110]_{\langle 001\rangle}$	$[2\ \ \xi\ \ \xi]$	[011]	$\langle 100\rangle$	3.04(6)*
TA $[110]_{\langle 1-10\rangle}$	$[2+\xi\ \ 2-\xi\ \ 0]$	[1–10]	$\langle 110\rangle$	2.63(10)

$$V(p) = V_0\left(1 + B_0'\frac{p}{B_0}\right)^{-1/B_0'}$$

where B_0 is a bulk modulus, B_0' is the first pressure derivative of the bulk modulus, and V_0 is a unit-cell volume at zero pressure. Fitting to the experimental data yields $V_0 = 233.3(7)$ Å^3, $B_0 = 19(1)$ GPa, and $B_0' = 3.1(3)$.

Since IXS has never been used to characterize lattice dynamics of hydrogen storage materials, we present the experimental results in more detail. In Fig. 3 we report on a few examples of the collected IXS spectra. These are characterized by an elastic contribution centered at zero energy and two symmetric features: the Stokes and anti-Stokes peaks of the acoustic phonons. The energy position $E(\mathbf{q})$ of the phonons was extracted using a model function composed of a sum of Lorentzian functions for which the inelastic contributions are constrained by the Bose factor. This model function was convoluted with the experimentally determined resolution function and fitted to the IXS spectra utilizing a standard χ^2 minimization routine. Momentum transfers used to obtain the complete picture of acoustic dispersion for high-symmetry directions are summarized in Table I. Intrinsic disorder of BH_4 tetrahedra[13] in the $Fm\bar{3}m$ phase should seriously influence inelastic scattering. Indeed, we have observed that (i) the elastic-scattering contribution never vanishes, (ii) the observed width of the central peak is larger than the resolution function, and (iii) substantial phonon peak broadening is observed far from the zone center. The broadening contributes as much as 3 meV to the FWHM [see Fig. 4(a)].

Phonon-dispersion relations extracted from the IXS experiment reproduce the overall shape of those derived from the theoretical calculation made for an ordered model ($F\bar{4}3m$ structure) but are much softer [Fig. 4(b)]. Elastic modules and bulk modulus derived from the slope of acoustic branches are shown in Table II together with the data from powder-diffraction and theoretical estimates.

The deviation of the IXS bulk modulus from the one derived from diffraction data can be understood if a small nonhydrostaticity occurs in the powder-diffraction experiments. Let us first neglect the shear strains as keeping the volume constant and assume the strain tensor to be in the following form:

$$\begin{bmatrix} \sigma(1-\alpha) & 0 & 0 \\ 0 & \sigma(1-\alpha) & 0 \\ 0 & 0 & \sigma(1+2\alpha) \end{bmatrix},$$

where α is a measure of the deviation from the hydrostatic condition. An apparent bulk modulus obtained from the compressibility measurements then reads

$$B_{\mathrm{XRD}} = \frac{1}{3}\frac{(C_{12}-C_{11})(C_{11}+2C_{12})}{C_{12}-C_{11}+\alpha C_{11}+2\alpha C_{12}} = \frac{C_{12}-C_{11}}{C_{12}-C_{11}+\alpha C_{11}+2\alpha C_{12}}B_{\mathrm{IXS}}.$$

Using the IXS elastic modules from Table II one easily estimates that $\alpha \approx 0.074$ brings diffraction data in agreement with the phonon dispersions. Such an anisotropy of the strain tensor is quite expected since all published diffraction data

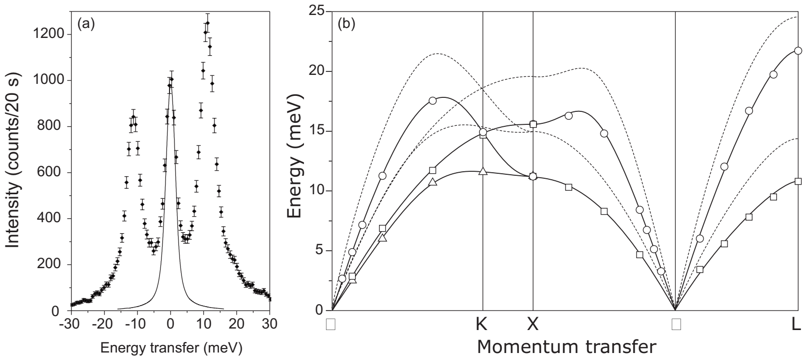

FIG. 4. (a) IXS spectrum recorded at (310) (solid diamonds) compared to the resolution function (solid line). (b) Phonon dispersion in high-symmetry directions; experimental points (empty symbols) connected by a guide for the eyes (solid lines) are compared with the *ab initio* calculations (dashed lines) for the $F\bar{4}3m$ structure (Ref. 6). The estimated experimental errors are less than the symbol size.

TABLE II. Elastic properties of $NaBH_4$ evaluated by different techniques.

	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)	B (GPa)
XRD				19 ± 1 [a]
				19.9[b]
IXS	26.5 ± 1.1	9.5 ± 0.57	9.4 ± 2.7	15.8 ± 1.8 [a]
Calculations				20.6[c]

[a] Data from this work.

[b] Data from previous diffraction experiments (Ref. 11).

[c] Results of *ab initio* calculations (Ref. 14).

have been measured without any pressure-transmitting media. Diffraction experiments with pressure cell without pressure media are known to give an overestimated bulk modulus (see Ref. 15 for more details).

The reason for the discrepancy between the theoretical estimates and the IXS value of 15.7 GPa is less clear. However, one generally expects different elasticity for the ordered approximant used in the density-functional theory (DFT) calculation and a real disordered system such as $NaBH_4$.[13] One could also note that unit-cell dimension obtained in Ref. 6 within the local-density approximation is substantially lower than the experimental one. Nevertheless, the IXS and DFT results shown in Fig. 4(b), being scaled, show nearly identical shapes of the dispersion curves.

IV. CONCLUSIONS

Dispersion relations for the acoustic phonons have been obtained for sodium borohydride using the IXS technique. Small crystals of natural isotope composition were used thus circumventing the natural limitations of inelastic neutron scattering. Comparison with the available experimental and theoretical information on the lattice dynamics and elasticity of $NaBH_4$ indicates (1) an overestimation of phonon frequencies in *ab initio* calculation and (2) overestimation of the bulk modulus derived from the high-pressure diffraction experiments. The latter fact can be explained by an apparent deviation from hydrostaticity; nonhydrostatic conditions are expected for the diffraction data, both previously published[11] and reported here, since the high reactivity of $NaBH_4$ prevents using the traditional pressure-transmitting media. Although the bulk moduli derived from the powder-diffraction data collected in nonhydrostatic conditions have to be taken with a grain of salt, correction for the preferred orientation effect, in agreement with published examples,[4] provides a good structural refinement.

With respect to the differences between the experimental and DFT results, both anharmonicity of thermal motion and static disorder are difficult to account for in DFT schemes used so far; therefore, unrealistic theoretical predictions of structural stability and thermodynamics have been done for light borohydrides (see $LiBH_4$ as an example).[16]

We have dealt with an experiment probing phonon dispersions in light borohydrides with IXS. It illustrates that phonons could be readily measured in light hydrogen storage materials and opens possibilities to study the dynamical response of these compounds to external stimuli. Together with the "static" information inherent to the diffraction experiments, the knowledge of lattice dynamics could lead to a coherent picture of physics and chemistry responsible for the hydrogen storage properties.

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