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# Elastic properties of $\text{NaXH}_4$ ( $X = \text{B}, \text{Al}$ )

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## Abstract

Elastic properties of  $\text{NaXH}_4$  ( $X = \text{B}, \text{Al}$ ) have been studied by first-principles calculations using a projected augmented plane-wave approach. The calculated elastic constants compare favorably with experimental values. Our calculations show that the theoretically calculated elastic constants and bulk moduli have small values compared with those of typical metals and intermetallic compounds, which indicates that  $\text{NaXH}_4$  ( $X = \text{B}, \text{Al}$ ) are highly compressible. Comparison of bulk moduli  $B$  of different complex hydrides shows a correlation between  $B$  and the decomposition temperatures. Also, we calculated the elastic anisotropies and the Debye temperatures from the elastic constants.

## 1. Introduction

The strong demand for new clean energy has intensified the interest in materials for energy storage. Complex hydrides have attracted much attention with their efficient hydrogen storage ability. These hydrides have been shown to hold higher hydrogen storage capability at moderate temperature and lower cost than conventional intermetallic hydrides. Among them,  $\text{NaBH}_4$  and  $\text{NaAlH}_4$  have received special attention for their high gravimetric hydrogen density. However, a serious problem with these materials is poor kinetics, high decomposition temperatures, and lacking reversibility with respect to hydrogen absorption/desorption.

Since Bogdanovic and Schwickardi [1] reported the reversibility of catalyzed hydrogen sorption reaction of  $\text{NaAlH}_4$ , many efforts have been devoted to study complex hydrides as hydrogen storage materials. There are mainly two ways for solving these problems. One is adding catalyst to the complex hydrides; the other is mixing two or more kinds of compounds, e.g.  $\text{LiBH}_4 + \text{LiNH}_3$  or  $\text{LiBH}_4 + \text{CaH}_2$  for decreasing the enthalpy changes. Unfortunately, the effects are limited in solving all of the three problems mentioned above. Moreover, the experimental efforts to finding an appropriate catalyst in complex hydrides cost too much, while theoretical calculations cost less. What we need is just an index for describing the catalytical effects. So more understanding of the basic material properties is still important for finding more efficient hydrogen storage methods.

Elastic properties of solids are important because they relate to various fundamental solid-state properties such as interatomic potentials, equation of state, and phonon spectra. Moreover, it is noticed that there is a correlation between the elastic constants and the melting temperatures of a solid [2, 3]; and the melting temperatures of  $\text{MBH}_4$  ( $M = \text{Li}, \text{Na}, \text{K}$ ) under hydrogen atmosphere can be regarded as an index of hydrogen decomposition temperatures, a concept applied in  $\text{MBH}_4$  ( $M = \text{Li}, \text{Na}, \text{K}$ ) successfully by Orimo *et al* [4]. Ravindran *et al* [5] have successfully calculated the Debye temperature of  $\text{TiSi}_2$  using elastic constants. So it is valuable to get the knowledge of elastic constants of  $\text{MXH}_4$  for determining their thermodynamic properties, e.g. decomposition temperature ( $T_d$ ). However, data for complex hydrides are much more limited. In particular, single-crystal elastic constants, which are required in the basic studies mentioned above, are not available except for a few cases [6]. Efforts have been made to calculate the elastic constants theoretically from so-called first-principles calculations and, although the bulk modulus has been calculated for various complex hydrides, calculations of elastic constants are relatively scarce [6].

In this paper, we present first-principles calculations of elastic constants of  $\text{NaXH}_4$  ( $X = \text{B}, \text{Al}$ ) and compare their melting temperatures ( $T_m$ ), bulk moduli  $B$ , and the distance of X–H ( $X = \text{Al}, \text{B}$ ) of different complex hydrides. We find a correlation between  $B$  and the melting temperature, from which we can theoretically predict the decomposition temperature ( $T_d$ ) in different conditions, such as under high pressure, doped by catalyst. Also, we describe the elastic anisotropy and Debye temperatures of  $\text{NaXH}_4$  ( $X = \text{B}, \text{Al}$ ).

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**Table 1.** Lattice constants (angstroms) and atom positions (in direct coordinates) of  $\text{MXH}_4$  ( $M = \text{Li}, \text{Na}$ ,  $X = \text{B}, \text{Al}$ ).

Compound	Lattice constants		Atomic coordinates	
$\alpha$ - $\text{NaBH}_4$ ( $F43m$ ) ( $Z = 4$ )	$a = 6.1480^a$	$a = 6.1183$	$\text{Na}(0, 0, 0)^a$ $\text{B}(0.5, 0.5, 0.5)^a$ $\text{H}(x, x, x)x = 0.3901^a$	$\text{Na}(0, 0, 0)$ $\text{B}(0.5, 0.5, 0.5)$ $\text{H}(x, x, x)x = 0.3846$
$\beta$ - $\text{NaBH}_4$ ( $P42_1c$ ) ( $Z = 2$ )	$a = 4.3464^b$ $c = 5.8620^b$	$a = 4.3455$ $c = 5.8725$	$\text{Na}(0, 0, 0)^b$ $\text{B}(0, 0, 0.5)^b$ $\text{H}(0.0111, 0.7694, 0.3803)^b$	$\text{Na}(0, 0, 0)$ $\text{B}(0, 0, 0.5)$ $\text{H}(0.0100, 0.7691, 0.3805)$
$\alpha$ - $\text{NaAlH}_4$ ( $I4_1/a$ ) ( $Z = 4$ )	$a = 4.9801^c$ $c = 11.1483^c$	$a = 5.0027$ $c = 11.1033$	$\text{Na}(0, 1/4, 1/8)^c$ $\text{Al}(0, 1/4, 5/8)^c$ $\text{H}(0.2372, 0.3869, 0.5456)^c$	$\text{Na}(0, 1/4, 1/8)$ $\text{Al}(0, 1/4, 5/8)$ $\text{H}(0.2653, 0.3589, 0.5810)$
$\beta$ - $\text{NaAlH}_4$ ( $Cmc2_1$ ) ( $Z = 4$ )	$a = 3.5493^d$ $b = 13.8304^d$ $c = 5.1133^d$	$a = 3.5298$ $b = 14.0151$ $c = 5.1021$	$\text{Na}(0, 0.1708, 0.2373)^d$ $\text{Al}(0, 0.4147, 0.2056)^d$ $\text{H1}(0, 0.3485, 0.4807)^d$ $\text{H2}(0, 0.3147, 0.0117)^d$ $\text{H3}(0, 0.0763, 0.6842)^d$ $\text{H4}(0, 0.5232, 0.3816)^d$	$\text{Na}(0, 0.1730, 0.2347)$ $\text{Al}(0, 0.4154, 0.2055)$ $\text{H1}(0, 0.3486, 0.4772)$ $\text{H2}(0, 0.3174, 0.0103)$ $\text{H3}(0, 0.0765, 0.6860)$ $\text{H4}(0, 0.5209, 0.3874)$

<sup>a</sup> Experiment [11]; <sup>b</sup> DFT [20]; <sup>c</sup> Experiment [9]; <sup>d</sup> DFT [10].

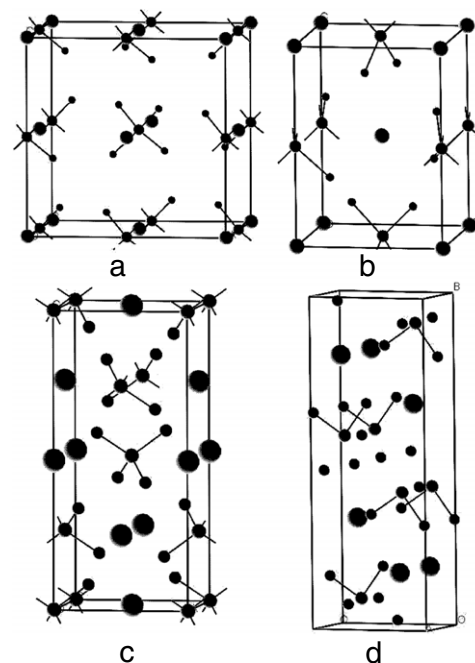
## 2. Computational details

To predict the ground-state crystal structure and elastic properties of  $\text{MXH}_4$ , the present calculations have been performed using the projected augmented plane-wave pseudopotentials (PAW) based on density functional theory implemented in the Vienna *ab initio* simulation package (VASP) [7, 8]. All calculations were carried out within the framework of the generalized gradient approximation (GGA) with Perdew–Wang 91 correlation functions. The cutoff energies are all 550 eV for  $\text{NaAlH}_4$ ,  $\text{NaBH}_4$ ; and the Monkhorst–Pack grid for Brillouin zone integration was chosen to achieve converged  $k$  meshes ( $5 \times 5 \times 2$  for  $\alpha$ - $\text{NaAlH}_4$ ,  $6 \times 2 \times 4$  for  $\beta$ - $\text{NaAlH}_4$ ,  $7 \times 7 \times 7$  for  $\alpha$ - $\text{NaBH}_4$ ,  $9 \times 9 \times 7$  for  $\beta$ - $\text{NaBH}_4$ ). The geometry optimizations have been done (ion coordinates and  $c/a$  ratio) by minimizing the Hellmann–Feynman forces on the atoms and total energy for the unit cell. In addition to the  $\alpha$ -phase of  $\text{NaXH}_4$  ( $X = \text{B}, \text{Al}$ ), we also calculated the elastic constants of the  $\beta$ -phase of  $\text{NaXH}_4$  ( $X = \text{B}, \text{Al}$ ) for comparison.

## 3. Results and discussion

The calculated lattice constants and atom positions of  $\text{NaXH}_4$  ( $X = \text{B}, \text{Al}$ ) are listed in table 1. Our theoretical values of  $\text{NaAlH}_4$  and  $\text{NaBH}_4$  are in good agreement with the experimental results and previous theory predictions for both lattice constants and atom positions [9–13], which indicates that our calculations are reliable. The optimized structures of  $\text{NaAlH}_4$  and  $\text{NaBH}_4$  are shown in figure 1. Our results indicate that  $[\text{BH}_4]^-$  and  $[\text{AlH}_4]^-$  anions in  $\alpha$ - $\text{NaXH}_4$  are tetrahedral. While Al atoms in  $\beta$ - $\text{NaAlH}_4$  have six nearest hydrogen atoms with Al–H distances of 1.54–1.81 Å. B–H and Al–H have strong covalent interactions and Na– $\text{BH}_4$  and Na– $\text{AlH}_4$  have ionic interactions [15].

For elastic constant calculations, the methods we used are described in [5]. The changes in total energy versus strain  $\delta$  for  $\text{NaXH}_4$  ( $X = \text{B}, \text{Al}$ ) were fitted with a quadratic function.



**Figure 1.** Upper row: crystal structure of (a)  $\alpha$ - $\text{NaBH}_4$ , (b)  $\beta$ - $\text{NaBH}_4$ . Lower row: (c)  $\alpha$ - $\text{NaAlH}_4$ , (d)  $\beta$ - $\text{NaAlH}_4$ .

### 3.1. Elastic constants

All of the calculated elastic constants of  $\text{NaXH}_4$  ( $X = \text{B}, \text{Al}$ ) are listed in table 2. The elastic constants of  $\text{NaBH}_4$  are found to compare favorably with the experimental values in [6], which indicates again that our calculation method is reliable. The experimental values of elastic constants of both  $\alpha$ - $\text{NaAlH}_4$  and  $\beta$ - $\text{NaAlH}_4$  are not available but our bulk moduli compare favorably with previous theoretical calculations [14].

The elastic constants  $C_{11}$ ,  $C_{22}$ , and  $C_{33}$  are important among all elastic constants, because they relate to the deformation behavior and atomic bonding characteristics of complex hydrides. For  $\alpha$ - $\text{NaAlH}_4$ ,  $C_{11} > C_{33}$  indicates that the atomic bonding along the (100) planes between nearest

**Table 2.** Elastic constants (GPa) of  $\text{MXH}_4$  ( $M = \text{Li, Na, X} = \text{B, Al}$ ).  $B_V$  and  $B_R$  denote Voigt bulk modulus and Reuss bulk modulus, respectively.  $G_V$  and  $G_R$  denote Voigt shear modulus and Reuss shear modulus, respectively.  $T_d$  (K) represents the decomposition temperature,  $T_m$  (K) represents the melting temperature.  $d_{X-H}$  represents the mean of distance between X and H in angstrom.

	NaBH <sub>4</sub> [6]	NaBH <sub>4</sub> ( <i>F43m</i> )	NaBH <sub>4</sub> ( <i>P42<sub>1</sub>c</i> )	NaAlH <sub>4</sub> ( <i>I4<sub>1</sub>/a</i> )	NaAlH <sub>4</sub> ( <i>Cmc2<sub>1</sub></i> )
$T_d$		838 <sup>a</sup>		483 <sup>b</sup>	
$T_m$		770 <sup>a</sup>		451 <sup>b</sup>	
$d_{\text{Na-X}}$	3.07	3.06		3.53	
$d_{X-H}$	1.17	1.17	1.22	1.63	1.68
$C_{11}$	26.5	30.2	38.0	39.7	94.5
$C_{12}$	9.5	13.4	6.2	10.6	14.5
$C_{13}$		13.4	13.6	5.0	29.1
$C_{22}$		30.2	38.0	39.7	44.1
$C_{23}$		13.4	13.6	5.0	15.9
$C_{33}$		30.2	40.8	29.7	66.6
$C_{44}$	9.4	12.4	9.5	11.5	80.6
$C_{55}$		12.4	9.5	11.5	36.2
$C_{66}$		12.4	6.7	13.5	20.4
$B_V$	15.2 <sup>c</sup>	19.0	20.4	16.7	36.0
$B_R$	15.2 <sup>c</sup>	18.6	15.2	16.1	31.6
$B$	15.8	18.8	17.8	16.4	33.8
$B$		7.6 <sup>d</sup>	7.8 <sup>d</sup>	19.3 <sup>e</sup>	36.5 <sup>e</sup>
$G_V$	9.0193 <sup>c</sup>	10.8	10.7	13.2	22.7
$G_R$	9.0353 <sup>c</sup>	10.4	9.0	13.0	17.5
$G$	9.0273 <sup>c</sup>	10.6	9.9	13.1	20.1

<sup>a</sup> Experimental values [26]; <sup>b</sup> experimental values [27]; <sup>c</sup> calculated from [6]; <sup>d</sup> DFT results [20].

<sup>e</sup> DFT results [10].

neighbors are stronger than those along the (001) planes. For  $\beta$ -NaAlH<sub>4</sub>, atomic bonding along the (100) plane is the strongest, next is atomic bonding along the (001) plane and (010) plane. These bonding characters are useful when considering their phase transitions under pressure or at high temperature.

As shown in table 2, the mean distances of X–H in the  $\beta$ -phase are shorter than those in the  $\alpha$ -phase, indicating that the interatomic bonding in the  $\beta$ -phase is stronger than that in the  $\alpha$ -phase. We find that the elastic constants of the  $\beta$ -phase are larger than those of the  $\alpha$ -phase except in a few cases ( $C_{11}$ ,  $C_{22}$ , and  $C_{33}$  in NaAlH<sub>4</sub>), which can be understood by the fact that the interatomic bonding in the  $\beta$ -phase is stronger than that in the  $\alpha$ -phase. As for the cases of  $C_{11}$ ,  $C_{22}$ , and  $C_{33}$  in NaAlH<sub>4</sub>, they can be explained by the fact that bonds along (001), (010), and (100) directions in the  $\beta$ -phase are stronger than those in the  $\alpha$ -phase.

Below, when we compare the properties of NaAlH<sub>4</sub> and NaBH<sub>4</sub>, we denote NaAlH<sub>4</sub> and NaBH<sub>4</sub> with 1 and 2 respectively for simplification. From table 2, we find that the order of the distance of X–H ( $X = \text{Al, B}$ ) is  $d_1 > d_2$ , which qualitatively indicates that covalent bonding in B–H is stronger than that in Al–H. One point to note is that doping the Ti cation into NaAlH<sub>4</sub> reduces the decomposition temperature of NaAlH<sub>4</sub>. This phenomenon can be explained with the distortion of tetrahedral AlH<sub>4</sub>. That is, the weakened Al–H bond will help reduce the decomposition temperature. Also, we find that the decomposition temperature varies inversely with  $d$  (X–H distance). We should note that the bulk modulus of NaBH<sub>4</sub> is larger than that of NaAlH<sub>4</sub> while  $d_{\text{B-H}}$  is shorter than  $d_{\text{Al-H}}$ , which can be understood by the fact that covalent bonding in BH<sub>4</sub> and AlH<sub>4</sub> is dominant in NaXH<sub>4</sub> ( $X = \text{B, Al}$ ) while bulk moduli reflect crystal bonding. The

relationship between  $B$  and the distance X–H (denoted by  $d$ ) suggested further studies on the relationship between  $B$  and the decomposition temperature. Melting temperatures of MBH<sub>4</sub> can be regarded as an index of hydrogen decomposition temperatures [4]. So, we can use melting temperature  $T_m$  rather than decomposition temperature  $T_d$  when discussing the relationship between  $B$  and the decomposition temperatures.

Fine *et al* [2] found a correlation between elastic constants and melting temperatures in metals and intermetallic compounds, e.g.  $T_m = 607 + 9.3B$ . Our results show a similar correlation. At least the tendency of melting temperature NaAlH<sub>4</sub> ( $T_m = 451$  K) < NaBH<sub>4</sub> ( $T_m = 770$  K) is the same as that of NaAlH<sub>4</sub> ( $B = 16.4$  GPa) < NaBH<sub>4</sub> ( $B = 18.8$  GPa). This interesting relation  $T_m = 132.9B - 1729$  (shown in figure 2) may be useful for predicting the decomposition temperature ( $T_d$ ) of doped MXH<sub>4</sub> qualitatively. The larger coefficient of this relationship is mainly from the fact that the differences of the elastic moduli are small in MXH<sub>4</sub> (e.g.  $\Delta T_m = 319$  K,  $\Delta B = 2.4$  GPa between NaAlH<sub>4</sub> and NaBH<sub>4</sub> while  $\Delta T_m = 301$  K,  $\Delta B = 28$  GPa between Ag and Al). Another factor influencing the coefficient of the relationship is the limited data of bulk moduli of MXH<sub>4</sub>. The exact relationship between  $T_m$  and elastic constants requires further computations and analysis.

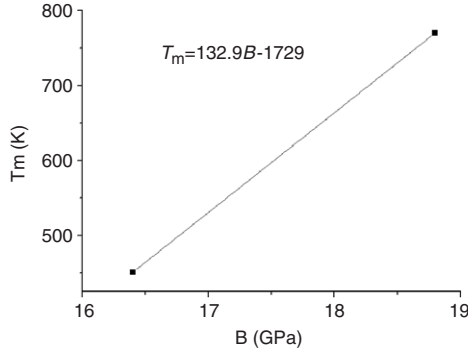
### 3.2. Bulk modulus, shear modulus, and Poisson's ratio

The difficulty in preparing the single-crystal samples leads to the impossibility of measuring the single-crystal elastic constants  $C_{ij}$ , while the bulk modulus  $B$  and shear modulus  $G$  can be determined more easily, so we give the results of  $B$  and  $G$  according to our calculated single-crystal elastic constants.

We calculated the shear modulus and bulk modulus using the Hill model, which takes the arithmetic average of the

**Table 3.** The calculated bulk modulus  $B$  (GPa), shear modulus  $G$  (GPa) and Poisson's ratio  $\nu$  of  $\text{MXH}_4$ .  $B_V$  and  $B_R$  denote the Voigt bulk modulus and Reuss bulk modulus, respectively.  $G_V$  and  $G_R$  denote the Voigt shear modulus and Reuss shear modulus, respectively.  $A$  is the Zener anisotropy index;  $A^U$  is the universal anisotropy index proposed by Ranganathan *et al* [24]. (Note: calculated from the experiment values of [6].)

Compound	$B$	$G$	$B/G$	$E$	$\nu$	$G_V/G_R$	$B_V/B_R$	$A^U$	$A$
$\alpha$ -NaAlH <sub>4</sub>	16.4	13.1	1.252	3.448	0.465	1.015	1.037	0.114	
$\beta$ -NaAlH <sub>4</sub>	33.8	20.1	1.682	5.592	0.472	1.297	1.139	1.625	
$\alpha$ -NaBH <sub>4</sub>	18.8	10.6	1.774	2.974	0.474	1.038	1.022	0.212	1.468
$\beta$ -NaBH <sub>4</sub>	17.8	9.9	1.798	2.784	0.474	1.189	1.342	1.286	



**Figure 2.** Relation between melting temperatures and bulk moduli.

Voigt [16] and Reuss models [17]. The Voigt shear modulus, Voigt bulk modulus, Reuss shear modulus, and Reuss bulk modulus are

$$G_V = \frac{1}{15}(C_{11} + C_{22} + C_{33} - C_{12} - C_{13} - C_{23}) + \frac{1}{5}(C_{44} + C_{55} + C_{66}) \quad (1)$$

$$B_V = \frac{1}{9}(C_{11} + 2C_{12} + 2C_{13} + C_{22} + 2C_{23} + C_{33}). \quad (2)$$

$$G_R = 15\{4(S_{11} + S_{22} + S_{33}) - 4(S_{12} + S_{13} + S_{23}) + 3(S_{44} + S_{55} + S_{66})\}^{-1} \quad (3)$$

$$B_R = \frac{1}{(S_{11} + S_{22} + S_{33}) - 2(S_{12} + S_{13} + S_{23})} \quad (4)$$

and the Hill bulk modulus and shear modulus are

$$B = \frac{1}{2}(B_R + B_V), \quad G = \frac{1}{2}(G_R + G_V). \quad (5)$$

The Young's modulus  $E$  and Poisson's ratio  $\nu$  [5] are given by

$$E = \frac{9BG}{3B + G} \quad \text{and} \quad \nu = \frac{3B - 2G}{2(3B + G)} = \frac{1}{2} \left( 1 - \frac{E}{3B} \right). \quad (6)$$

The calculated bulk modulus,  $B$ , shear modulus,  $G$ , Young's modulus,  $E$ , and Poisson's ratio for  $\text{NaXH}_4$  are given in table 3, from which we find that the calculated bulk moduli are much smaller than for typical metals [18] and intermetallic compounds [19], which indicates that all  $\text{NaXH}_4$  ( $X = \text{B}, \text{Al}$ ) are highly compressible materials as also shown in [20]. The bulk modulus of  $\text{NaBH}_4$  is larger than that of  $\text{NaAlH}_4$ , indicating that the bonding in  $\text{NaBH}_4$  is stronger than that in  $\text{NaAlH}_4$ . The larger value of shear modulus is an indication of the more pronounced directional bonding between atoms.

The larger value of shear modulus of  $\alpha$ - $\text{NaAlH}_4$  compared to that of  $\alpha$ - $\text{NaBH}_4$  indicates that the bonding behavior of  $\alpha$ - $\text{NaAlH}_4$  is more directional than that of  $\alpha$ - $\text{NaBH}_4$ . In fact the discussions about elastic anisotropy in section 3.3 prove this conclusion again. Pugh [21] introduced the quotient of bulk to shear modulus of polycrystalline phases ( $B/G$ ) as a measure of ductility by considering that the shear modulus  $G$  represents the resistance to plastic deformation while the bulk modulus represents the resistance to fracture. Higher ( $B/G$ ) value is associated with higher ductility and the critical value which separates ductile and brittle materials is 1.75. It is interesting that  $\text{NaBH}_4$  is ductile while  $\text{NaAlH}_4$  is brittle. Moreover, the ratios  $B/G$  increase by 1% for  $\text{NaAlH}_4$  and by 26% for  $\text{NaBH}_4$  when  $\alpha$ - $\text{NaXH}_4$  transforms into  $\beta$ -phase.

Poisson's ratio is associated with the volume change during uniaxial deformation. The low  $\nu$  value for  $\text{MXH}_4$  means a large volume change occurs during elastic deformation and  $\nu = 0.5$  means no volume change occurs. The  $\nu(0.465)$  in  $\text{NaAlH}_4$  is smaller than that (0.473) in  $\text{NaBH}_4$ , indicating that  $\text{NaAlH}_4$  has more volume change during uniaxial deformation. In addition, more information can be found about the characteristics of the bonding forces from Poisson's ratio than any other elastic constants [22]. It has been proved that  $\nu = 0.25$  is the lower limit for central-force solids and 0.5 is the upper limit, which corresponds to infinite elastic anisotropy [23]. Our calculations suggest that both  $\text{NaAlH}_4$  and  $\text{NaBH}_4$  are central-force solids.

### 3.3. Elastic anisotropy

Crystal anisotropy reflects the different atomic arrangement in different directions, which results in different bonding character and affects the physical and chemical properties in different directions of materials. Here, we describe the elastic anisotropy using the anisotropy index proposed by Ranganathan and Ostojica-Starzewski [24]. The universal anisotropy index is

$$A^U = 5 \frac{G_V}{G_R} + \frac{B_V}{B_R} - 6. \quad (7)$$

$G_V$ ,  $G_R$ ,  $B_V$  and  $B_R$  denote Voigt shear modulus, Reuss shear modulus, Voigt bulk modulus, and Reuss bulk modulus respectively. For isotropic single crystals  $A^U$  is zero, while the departure of  $A^U$  from zero defines the extent of single-crystal anisotropy and accounts for both the shear and bulk

**Table 4.** Molecular mass ( $M$ ) with the density ( $\rho$  in  $\text{g cm}^{-3}$ ), longitudinal, transverse, average elastic wavevelocity ( $v_l, v_t, v_m$  in  $\text{m s}^{-1}$ ), and the Debye temperatures  $T_D$  (K) calculated from our results.

Compound	$M$	$\rho$	$B$	$G$	$v_l$	$v_t$	$v_m$	$T_D^a$	$T_D^b$
$\alpha\text{-NaAlH}_4 (Z = 4)$	54.00	1.170	16.4	13.1	7090	3346	4528	577	
$\beta\text{-NaAlH}_4 (Z = 4)$	54.00	1.288	33.8	20.1	7176	4201	4658	613	
$\alpha\text{-NaBH}_4 (Z = 4)$	37.83	1.013	18.8	10.6	5200	2987	3318	454	528
$\beta\text{-NaBH}_4 (Z = 2)$	37.83	1.101	17.8	9.9	5306	2999	3336	591	

<sup>a</sup> Calculated from  $B, G$ ; <sup>b</sup> calculated from  $C_{ij}$ .

contributions [24]. For comparison, we give another anisotropy index  $A$  proposed by Zener [25] for  $\alpha\text{-NaBH}_4$

$$A = \frac{2C_{44}}{C_{11} - C_{12}}. \quad (8)$$

The calculated elastic anisotropies index  $A$  and  $A^U$  are listed in table 3. For  $\text{NaXH}_4$ , the  $\beta$ -phase is more anisotropic than the  $\alpha$ -phase, which can be understood by the fact that the bonding of the  $\beta$ -phase differs significantly in different directions (e.g. the length difference between the  $c$  axis and  $a$  axis is almost 35% in  $\beta\text{-NaBH}_4$ ).  $\alpha\text{-NaBH}_4$  is more anisotropic than  $\alpha\text{-NaAlH}_4$  and the difference is mainly the contribution of shear bulk modulus.

### 3.4. Calculation of Debye temperature

Thermal conductivity measurement is useful for predicting phase transitions [30]. The thermal conductivity coefficient is proportional to specific heat, which can be calculated from Debye temperature in the Debye model. Debye temperature is associated with many physical properties of solids, such as specific heat, elastic constants, and the melting temperature [5]. At low temperatures the vibrational excitations arise solely from acoustic vibrations. Hence, we can calculate the Debye temperature from elastic constants rather than measure it from specific heat at low temperature. Debye temperature ( $T_D$ ) may be determined from average sound velocity,  $v_m$ , by

$$T_D = \frac{h}{k} \left[ \frac{3n}{4\pi} \left( \frac{N_A \rho}{M} \right) \right]^{1/3} v_m, \quad (9)$$

where  $h$  is Planck's constant,  $k$  is Boltzmann's constant,  $N_A$  is Avogadro's number,  $\rho$  is the density of the molecule,  $M$  is the molecular weight, and  $n$  is the number of atoms in the molecule. The average velocity  $v_m$  in the polycrystalline materials is approximately given by

$$v_m = \left[ \frac{1}{3} \left( \frac{2}{v_l^3} + \frac{1}{v_t^3} \right) \right]^{-1/3}, \quad (10)$$

where  $v_l$  and  $v_t$  are longitudinal and transverse elastic velocity and may be obtained from Navier's equation

$$v_l = \left( \frac{B + \frac{4G}{3}}{\rho} \right)^{1/2} \quad (11)$$

and

$$v_t = \left( \frac{G}{\rho} \right)^{1/2}. \quad (12)$$

The calculated  $\rho, v_l, v_t, v_m$ , and  $T_D$  are listed in table 4. We find that the Debye temperature of the  $\beta$ -phase is higher than those of the  $\alpha$ -phase, which is consistent with the conclusion of [28], in which Talyzin *et al* conclude there is a large increase of Debye temperature according to the large increase of thermal conductivity when phase transition occurs.

The Debye temperature  $T_D$  can be calculated directly from elastic constants by [29]

$$\frac{3}{\theta_D} = \frac{1}{\theta_l} + \frac{2}{\theta_t}$$

where

$$\theta_l = \frac{h v_l}{k_B} \quad \text{and} \quad \theta_t = \frac{h v_t}{k_B}$$

where  $h$  is Planck's constant,  $k_B$  is Boltzmann's constant.  $v_l$  and  $v_t$  are longitudinal and transverse frequencies of the elastic wave and can be obtained by

$$v_l = U_l \left( \frac{3N}{4\pi V} \right)^{1/3}, \quad v_t = U_t \left( \frac{3N}{4\pi V} \right)^{1/3}$$

where  $U_l, U_t$  are longitudinal and transversal velocities and can be obtained by solving the Christoffel equation. For  $\alpha\text{-NaBH}_4$ ,  $U_l$  and  $U_t$  are

$$U_l = \left( \frac{C_{11}}{\rho} \right)^{1/2}, \quad U_t = \left( \frac{C_{44}}{\rho} \right)^{1/2}.$$

We calculated the Debye temperature of  $\alpha\text{-NaBH}_4$  using this method and compared it with that calculated from  $B, G$ . From table 4, we find that the Debye temperature calculated directly from  $C_{ij}$  is higher than that calculated from  $B, G$ . The difference is mainly from the fact that  $C_{ij}$ - $B, G$  conversion already represents some kind of averaging, which is not equivalent to Debye-model averaging.

## 4. Conclusions

We have performed first-principles calculations of elastic constants of  $\text{NaXH}_4$  ( $X = \text{B, Al}$ ) and find values of  $B$  may be used to predict qualitatively the decomposition temperatures of  $\text{NaXH}_4$ . The increase of  $B$  leads to an increase of decomposition temperature. This may be explained by the shortened distance of X-H, leading to weaker covalent-bond strength of X-H. Our results are useful for predicting decomposition temperature under different conditions e.g. doped by catalyst. We find that all the bulk moduli are small, which indicates that  $\text{MXH}_4$  are high-compressibility materials. Other elastic constants are

also small compared with values of typical metals. Elastic constants of the  $\beta$ -phase are larger than those of the  $\alpha$ -phase, which can be explained by the fact that bonding in the  $\beta$ -phase is stronger. We also discuss elastic anisotropy of different complex hydrides. We find that our DFT results for  $\text{NaBH}_4$  predict larger anisotropy than experiment. The Debye temperatures have been calculated from average elastic wave velocities obtained from shear and bulk moduli and directly from elastic constants  $C_{ij}$ .

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