

## Pressure-induced phase of NaAlH<sub>4</sub>: A potential candidate for hydrogen storage?

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The electronic structure and structural stability of the technologically interesting material NaAlH<sub>4</sub> are studied using an *ab initio* projected augmented plane-wave method for different possible structure modifications. We predict that  $\alpha$ -NaAlH<sub>4</sub> converts to  $\beta$ -NaAlH<sub>4</sub> at 6.43 GPa with a 4% volume contraction. Both modifications have nonmetallic character with finite energy gaps, the calculated band gap for  $\beta$ -NaAlH<sub>4</sub> being almost half of that for the  $\alpha$  phase.  $\beta$ -NaAlH<sub>4</sub> stores hydrogen more volume efficient than the  $\alpha$  phase and would if stabilized at ambient conditions be an interesting candidate for further studies with regard to hydrogen absorption/desorption efficiency. © 2003 American Institute of Physics. [DOI: 10.1063/1.1566086]

Introduction of “hydrogen economy” requires safe and efficient storage of hydrogen, and hence, potential solid storage materials have been intensively studied for several decades. The hitherto known hydrides with high capacity for potential reversible hydrogen storage are hampered by thermodynamic and kinetic limitations. Interstitial hydrides (based on *AB*, *AB*<sub>2</sub>, and *AB*<sub>5</sub> transition-metal intermetallics) are easily reversible at around room temperature, but the relative weight of stored hydrogen is limited (1.5–2.5 wt %).<sup>1,2</sup> In contrast, MgH<sub>2</sub> and LiH have a high relatively H content (7–13 wt %), but owing to the presence of strong ionic/covalent bonding interactions, the desorption temperature is high (>250 °C). In the search for suitable materials for reversible hydrogen storage, alkali aluminum hydrides such as NaAlH<sub>4</sub> and LiAlH<sub>4</sub> have attracted interest mainly due to the high relative weight of stored hydrogen (7.5 and 10.6 wt %, respectively). Recently Bogdanovic and co-workers<sup>3,4</sup> have established that sodium aluminum hydrides, which were earlier considered in actual practice as irreversible with respect to hydrogen absorption/desorption, could be made reversible by doping with Ti. Efforts<sup>5,6</sup> have also been made to improve the hydrogen reversibility of NaAlH<sub>4</sub> by ball milling in combination with (or without) additives. In line with this, considerable interest is attached to the structural properties of NaAlH<sub>4</sub> at higher pressures, but no experimental or theoretical high-pressure studies have hitherto been performed. A theoretical investigation of NaAlH<sub>4</sub> is also of topical interest because of the difficulties involved in establishing the location of the hydrogen atoms by high-pressure diffraction techniques.

At ambient conditions NaAlH<sub>4</sub> crystallizes in the tetragonal structure<sup>7,8</sup> shown in Fig. 1(a) (space group *I*4<sub>1</sub>/*a*). The [AlH<sub>4</sub>]<sup>−</sup> anion has a compressed tetrahedral geometry with Al–H distances of 1.603 Å. The Na<sup>+</sup> cation has eight nearest H neighbors which define the vertices of a distorted triangular dodecahedron. Related compounds with the same stoichiometry take rather different structures: LiBH<sub>4</sub> (hexagonal-*P*6<sub>3</sub>*m*c),<sup>9</sup> NaGaH<sub>4</sub> (orthorhombic-*Cmcm*),<sup>10</sup>

NaBH<sub>4</sub> (cubic-*Fm*3*m*),<sup>11</sup> LiAlH<sub>4</sub> (monoclinic-*P*2<sub>1</sub>/*c*),<sup>12</sup> KGaH<sub>4</sub> (orthorhombic-*Pnma*),<sup>13</sup> and SrMgH<sub>4</sub> (orthorhombic-*Cmc*2<sub>1</sub>).<sup>14</sup> The present theoretical study includes the actually established structure for NaAlH<sub>4</sub> as well as the just mentioned six potential alternatives.

Total energies have been calculated by the projected augmented plane-wave<sup>15</sup> implementation of the Vienna *ab initio* simulation package.<sup>16</sup> The generalized gradient approximation<sup>17</sup> were used to obtain accurate exchange and correlation energies for a particular ionic configuration. The structures are fully relaxed for all volumes considered in the present study using force as well as stress minimization. Experimentally established structural data were used as input for the calculations when available. For the tetragonal NaAlH<sub>4</sub> structure we used 432 **k** points in the whole Brillouin zone. A similar density of **k** points was used for the other structures. In order to avoid ambiguities regarding the free-energy results we have used the same energy cutoff and similar **k**-grid densities in all calculations. At least 0.01 meV/atom was placed as a criterion on the self-consistent conver-

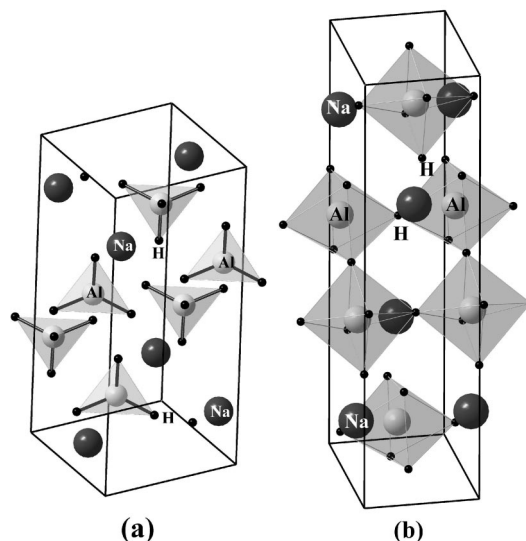


FIG. 1. Crystal structure of (a)  $\alpha$ -(tetragonal-*I*4<sub>1</sub>/*a*) and (b)  $\beta$ -NaAlH<sub>4</sub> (SrMgH<sub>4</sub>-type; orthorhombic-*Cmc*2<sub>1</sub>).

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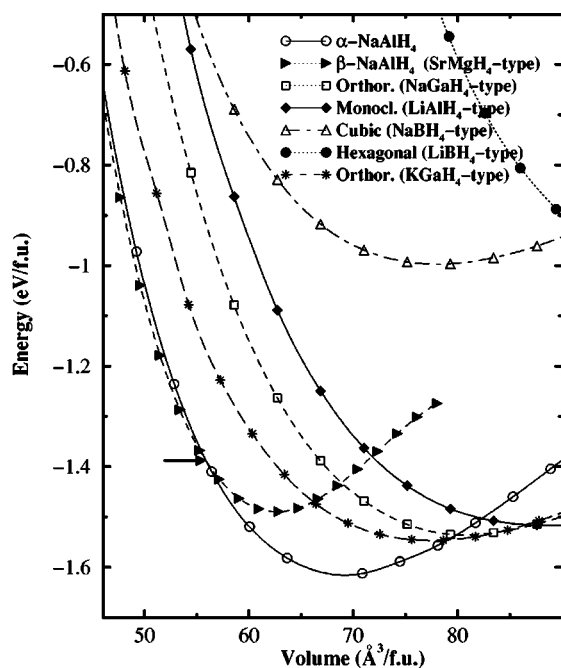


FIG. 2. Calculated unit-cell volume vs free energy for  $\text{NaAlH}_4$  in different structural arrangements. Arrow marks the  $\alpha \rightarrow \beta$  transition.

gence of the total energy, and the calculations reported here used a plane wave cutoff of 600 eV. The zero-point entropy contribution to the free energy has not been included in the calculations, but its contribution should in any case be very small and should not affect transition pressures significantly.<sup>18</sup> A similar approach was successfully applied in the case of  $\text{MgH}_2$ , where the three experimentally observed high-pressure phases were reproduced rather well.<sup>19</sup>

In agreement with the experimental findings,<sup>7,8</sup> the actual tetragonal structure takes the lowest energy (Fig. 2) among the seven considered phases. Hence, at ambient conditions  $\text{NaAlH}_4$  crystallizes in the tetragonal structure (hereafter named as the  $\alpha$  phase) with lattice constants  $a = 4.9965$  and  $c = 11.0828$  Å, [close (within 1%) to the low-temperature (8 K) experimental values<sup>8</sup> of  $a = 4.9801$  and  $c = 11.1483$  Å]. Similarly the calculated atomic coordinates for  $\alpha$ - $\text{NaAlH}_4$  are in good agreement with experimental findings (Table I). At higher pressures,  $\alpha$ - $\text{NaAlH}_4$  transforms to an orthorhombic  $\text{SrMgH}_4$ -type structure [space group  $Cmc2_1$  [Figs. 1(b) and 2]; hereafter  $\beta$ - $\text{NaAlH}_4$ ]. The coordination number (CN) of Al changes from 4 in  $\alpha$ - $\text{NaAlH}_4$  to 6 in the  $\beta$  phase, *viz.* consistent with the expected general trend of increasing CN with weakening of the covalent/ionic bonding with increasing pressure. We have calculated the total energy as a function of unit-cell volume for 12 different volumes and fitted the results to the so-called universal equation state<sup>20</sup> and thus obtained bulk moduli ( $B_0$ ) and pressure derivatives ( $B'_0$ ) for  $\alpha$ - and  $\beta$ - $\text{NaAlH}_4$ . Both phases have low bulk moduli ( $B_0 = 19.3$  and 36.5 GPa;  $B'_0 = 4.77$  and 3.78, respectively) implying that  $\text{NaAlH}_4$  is a very soft and easily compressible material.  $B_0$  for  $\beta$ - $\text{NaAlH}_4$  is almost twice that of the  $\alpha$  phase, largely due to the increased CN and the lower equilibrium volume of  $\beta$ - $\text{NaAlH}_4$ .

The theoretically generated pressure-volume curve (Fig. 3) shows that  $\alpha$ - $\text{NaAlH}_4$  is converted into the  $\beta$  phase at 6.43 GPa with a volume reduction of  $\sim 4\%$ . In order to

TABLE I. Optimized structural parameters for  $\alpha$ -(tetragonal  $I4_1/a$ ) and  $\beta$ - $\text{NaAlH}_4$  ( $\text{SrMgH}_4$ -type; orthorhombic  $Cmc2_1$ ).

Phase	Unit cell (Å)	Atomic coordinates
$\alpha$	$a = 4.9965$	Na: 0, 1/4, 1/8;
	$= 4.9801^a$	Al: 0, 1/4, 5/8;
	$c = 11.0828$	H: 0.2199, 0.3710, 0.5639
	$= 11.1483^a$	0.2372, <sup>a</sup> 0.3869, <sup>a</sup> 0.5456 <sup>a</sup>
$\beta$	$a = 3.5493$	Na: 0, 0.1708, 0.2373 (0, 0.1695, 0.2409); <sup>b</sup>
	$b = 13.8304$	Al: 0, 0.4147, 0.2056 (0, 0.4139, 0.2047); <sup>b</sup>
	$c = 5.1133$	H(1): 0, 0.3485, 0.4807 (0, 0.3476, 0.4877); <sup>b</sup>
		H(2): 0, 0.3147, 0.0117 (0, 0.3105, 0.0116); <sup>b</sup>
		H(3): 0, 0.0763, 0.6842 (0, 0.0751, 0.6811); <sup>b</sup>
		H(4): 0, 0.5232, 0.3816 (0, 0.5269, 0.3739) <sup>b</sup>

<sup>a</sup>Experimentally observed values from Ref. 8.

<sup>b</sup>Atomic coordinates at transition point (in parentheses).

obtain a clearer picture of the conditions at the transition point and the possibility for formation of the  $\beta$  phase, we show the pressure dependence of the Gibbs free energy difference ( $\Delta G$ ) between the  $\alpha$ - and  $\beta$ - $\text{NaAlH}_4$  in the inset to Fig. 3. The calculated total-energy difference (Fig. 2) between the two structures at their equilibrium volumes is only 126 meV/f.u. (12.2 kJ/mol). The equilibrium volume of  $\beta$ - $\text{NaAlH}_4$  at 1 bar is 9% smaller than that of the  $\alpha$  phase (see Fig. 2), indicating that hydrogen can be stored more efficiently in the  $\beta$  phase. At higher pressures the involved energy difference between  $\alpha$ - and  $\beta$ - $\text{NaAlH}_4$  is small. In line with the findings for  $\text{TiO}_2$ <sup>21</sup> one should search for possibilities to stabilize the high-pressure phase  $\beta$ - $\text{NaAlH}_4$  at ambient pressure by appropriate treatment (perhaps by chemical means, that moreover may open up for improved reversible hydrogen absorption/desorption kinetics).

The calculated density of states (DOS) for  $\alpha$ - $\text{NaAlH}_4$  (at equilibrium) and  $\beta$ - $\text{NaAlH}_4$  (at transition pressure) are shown in Fig. 4. Both phases have nonmetallic character with finite band gaps ( $\Delta E_g \approx 5.04$  and 2.35 eV for  $\alpha$ - and  $\beta$ - $\text{NaAlH}_4$ , respectively). The energetic degeneration of the

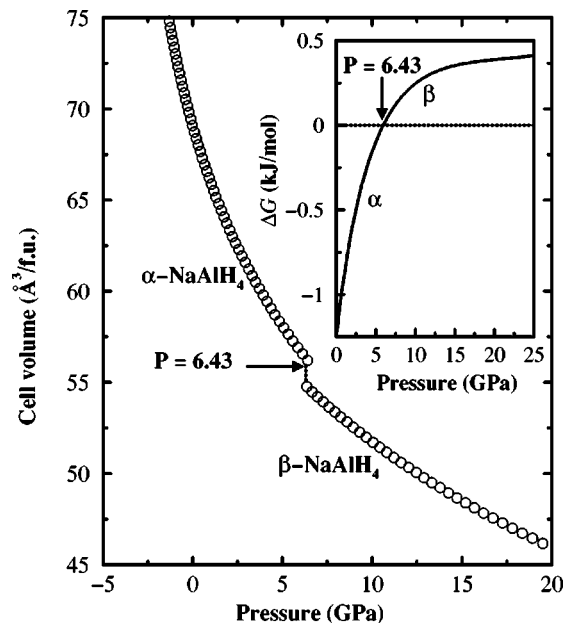


FIG. 3. Pressure-volume relationship for  $\text{NaAlH}_4$ . Inset: Stability of  $\alpha$ - $\text{NaAlH}_4$  relative to  $\beta$ - $\text{NaAlH}_4$  in terms of pressure. Arrows mark the transition pressure.

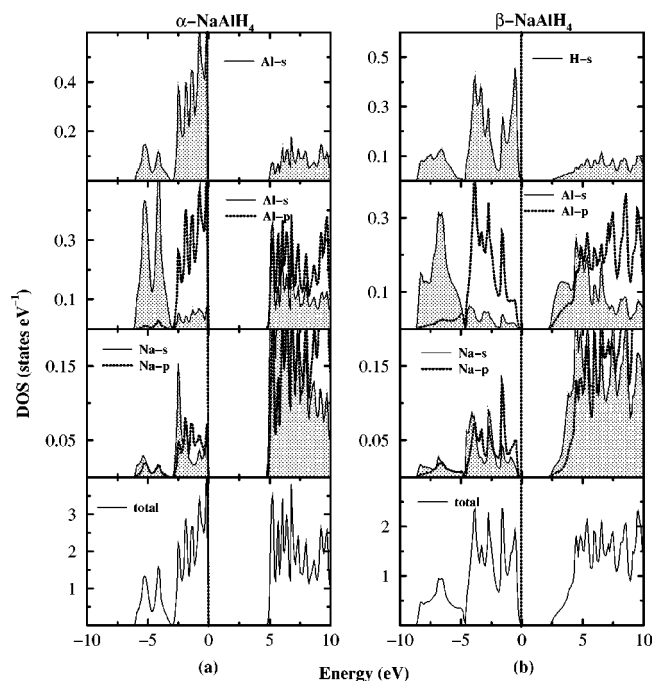


FIG. 4. Calculated DOS for (a)  $\alpha$ - and (b)  $\beta$ -NaAlH<sub>4</sub>. The Fermi level is set at zero energy and marked by the vertical lines, *s* electron contributions are marked with dotted regions.

Al-*p* and H-*s* states together with a spatially favorable constellation of Al and H facilitate covalent bonding between Al and H.  $\Delta E_g$  for  $\beta$ -NaAlH<sub>4</sub> is only about half of that for  $\alpha$ -NaAlH<sub>4</sub> and there are significant differences between the DOS for the two phases, especially the broadening and shifting of the bands. The partial DOS of Na shows that the *s* and *p* states are energetically degenerate in the whole energy range, while Al-*s* and -*p* states are well separated in both phases.

On going from  $\alpha$ - to  $\beta$ -NaAlH<sub>4</sub> the width of the valence band is increased from 6 to 8 eV, which is partially due to the decrease in the interatomic Al–H, Al–Na, and Na–H distances. Moreover, owing to the increase in the hybridization of Al-*p* with H-*s* at elevated pressures, the center of the Al-*p* band is shifted from  $\sim -1.5$  eV in  $\alpha$ -NaAlH<sub>4</sub> to  $\sim -3.5$  eV in the  $\beta$  phase. The reduction in the band gap and the increase in the CN of the  $\beta$  phase indicate that the tendency toward metallic nature increases with pressure. Hence, one could expect appreciable differences in the kinetics of the hydrogen-storage properties of the  $\alpha$  and  $\beta$  phases.

In conclusion, on application of pressure  $\alpha$ -NaAlH<sub>4</sub> is predicted to transform into a  $\beta$  phase at 6.43 GPa with a 4% volume reduction. The calculated structural parameters for

$\alpha$ -NaAlH<sub>4</sub> are in good agreement with the experimental values. Both  $\alpha$ - and  $\beta$ -NaAlH<sub>4</sub> have nonmetallic character with finite band gaps. The coordination number of Al in  $\beta$ -NaAlH<sub>4</sub> is six as compared with four for  $\alpha$ -NaAlH<sub>4</sub>. At the high pressures where  $\beta$ -NaAlH<sub>4</sub> rules, the Al-*p* states are more delocalized and the large DOSs at the top of the VB are moved to lower energies compared with the  $\alpha$  phase. This leads to a gain in the band-energy contribution to the total energy with pressure, and this may be the reason for the  $\alpha$ -to- $\beta$  phase transition.

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