$Ca(AlH_4)_2$, $CaAlH_5$, and $CaH_2+6LiBH_4$: Calculated dehydrogenation enthalpy, including zero point energy, and the structure of the phonon spectra

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(Received 28 March 2008; accepted 9 May 2008; published online 17 June 2008)

The dehydrogenation enthalpies of $Ca(AlH_4)_2$, $CaAlH_5$, and $CaH_2+6LiBH_4$ have been calculated using density functional theory calculations at the generalized gradient approximation level. Harmonic phonon zero point energy (ZPE) corrections have been included using Parlinski's direct method. The dehydrogenation of $Ca(AlH_4)_2$ is exothermic, indicating a metastable hydride. Calculations for $CaAlH_5$ including ZPE effects indicate that it is not stable enough for a hydrogen storage system operating near ambient conditions. The destabilized combination of $LiBH_4$ with CaH_2 is a promising system after ZPE-corrected enthalpy calculations. The calculations confirm that including ZPE effects in the harmonic approximation for the dehydrogenation of $Ca(AlH_4)_2$, $CaAlH_5$, and $CaH_2+6LiBH_4$ has a significant effect on the calculated reaction enthalpy. The contribution of ZPE to the dehydrogenation enthalpies of $Ca(AlH_4)_2$ and $CaAlH_5$ calculated by the direct method phonon analysis was compared to that calculated by the frozen-phonon method. The crystal structure of $CaAlH_5$ is presented in the more useful standard setting of $P2_1/c$ symmetry and the phonon density of states of $CaAlH_5$, significantly different to other common complex metal hydrides, is rationalized. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2937917]

I. INTRODUCTION

Hydrogen is widely regarded as an attractive alternative to fossil fuels for transport and other mobile applications, being lightweight, nontoxic, and producing only water at the point of end use. The lack of suitable high density storage remains one of the main problems holding back practical implementations.[1] Though many storage systems have been proposed, no currently known system meets desired targets of storage density, hydrogen availability, and energy efficiency, let alone cost. Chemical hydrides show much promise, but the (de)hydrogenation kinetics for these systems needs to be improved.

A decade ago, Bogdanovic and Schwickardi found that the hydrogenation and dehydrogenation kinetics and storage reversibility of $NaAlH_4$ are significantly improved by adding small amounts of Ti.[2] In light of this, light element complex metal hydrides (especially the alanates) are promising materials for practical hydrogen storage. In general light element complex metal hydrides have high volumetric and gravimetric hydrogen densities, essential properties for mobile applications.

$Ca(AlH_4)_2$ is one such high hydrogen density alanate, exhibiting 7.9 wt % hydrogen content in total. It decomposes to CaH_2 in a two-step process with the formation of a $CaAlH_5$ intermediate in the first step, as indicated in reactions (1) and (2).[3–5] Overall the decomposition can be described as reaction (3). The intermediate $CaAlH_5$ phase has been identified only recently. Thus many researchers have neglected the two step mechanism, considering only reaction (3);

$$Ca(AlH_4)_2 \rightarrow CaAlH_5 + Al + 3/2H_2, \quad (1)$$

$$CaAlH_5 \rightarrow CaH_2 + Al + 3/2H_2, \quad (2)$$

$$Ca(AlH_4)_2 \rightarrow CaH_2 + 2Al + 3H_2. \quad (3)$$

The ground state $Ca(AlH_4)_2$ crystal structure of space group *Pbca* has been determined by density functional theory (DFT) band-structure calculations,[6] with the simulated x-ray diffraction pattern agreeing well with the powder pattern subsequently measured.[7] The crystal structure of $CaAlH_5$ has also been predicted using DFT calculations, revealing a α'-$SrAlF_5$-type crystal structure of $P2_1/n$ symmetry. Like $Ca(AlH_4)_2$ before it, this theoretical prediction was confirmed by the successful refinement of the structure from measured x-ray diffraction patterns.[7] The intermediate $CaAlH_5$ is the first pentahydride known in the family of complex metal hydrides, in which tetrahydrides and hexahydrides abound.

The energy changes for reactions (1)–(3) have previously been calculated by one of the present authors without including the zero point energy (ZPE).[7] These calculations indicate that the first step, reaction (1), is exothermic, and

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thus irreversible. The second step, reaction (2), is a candidate hydrogen storage system in its own right since 4.2 wt % of H_2 can be released from $CaAlH_5$ via reaction (2) (without decomposing the relatively stable CaH_2 product). The dehydrogenation energy for the second step is calculated to be 39.9 kJ/mole H_2 without the ZPE contribution. This value lies within the target range for hydrogen storage materials.[1]

It is now well known that including ZPE effects (in the harmonic approximation) for the dehydrogenation of complex metal hydrides has a significant effect on the calculated reaction enthalpy.[8–12] Including ZPE contributions typically reduces the calculated energy change by 10–20 kJ/mol H_2,[8] a range sufficiently predictable that it can be used to speed potential hydrogen storage system screening.[13]

Wolverton and Ozoliņš have calculated the ZPE corrected dehydration enthalpies for reactions (1)–(3) using the frozen-phonon method.[14] The calculated energies of decomposition were found to be −4.8, 29.8, and 12.2 kJ/mole H_2 for reactions (1)–(3), respectively, without including the ZPE contribution. According to these published results, by including the ZPE change the decomposition enthalpies decrease by 7–14 kJ/mol H_2. Thus reaction (1) is calculated to be even more exothermic, whereas reactions (2) and (3) remain endothermic with a dehydrogenation energy reduced from that previously calculated as the change in potential energy.

Alapati *et al.* have calculated the dehydration enthalpies for many destabilized hydride systems,[15] initially without including ZPE in their study. One of the reactions studied with an enthalpy change that appears to be favorable for hydrogen storage applications is a mixture of CaH_2 with $LiBH_4$, reaction (4). The energy change for this reaction is calculated to be 62.7 kJ/mol H_2.[15]

$$CaH_2 + 6LiBH_4 \rightarrow CaB_6 + 6LiH + 10H_2. \quad (4)$$

In a subsequent paper, Alapati *et al.* extend their reaction set to over 340 possible combinations of materials.[16] Vibrational effects are included for a number of promising destabilized hydride systems, including reaction (4) above. For this reaction, including ZPE reduces the calculated dehydrogenation enthalpy by 20.3 kJ/mol H_2 to 42.4 kJ/mol H_2. In the work of Alapati *et al.* the ZPE contribution to the dehydration enthalpies were calculated using Parlinski's direct method.[17]

In the present work, we have calculated ZPE corrections using the direct method for reactions (1) and (2), and thus for the more often considered reaction (3). We have also repeated the calculations performed by Alapati *et al.*[16] on reaction (4) as a representative sample of their ZPE-corrected values for mixed hydride systems. The aims of this work are twofold. First, we aim to independently confirm the published results of Alapati *et al.*[16] and Wolverton and Ozoliņš.[14] Second, not only do we aim to perform an independent validation of the dehydrogenation enthalpies of the calcium alanates, we also aim to perform a practical comparison between the ZPE corrections calculated using the direct method (that is becoming widely used in hydrogen storage material research) with the older frozen-phonon approach that has been used by Wolverton and Ozoliņš.[14]

II. METHOD

Plane wave DFT[18] was used to calculate potential energies using the program VASP.[19] The PW91 generalized gradient approximation exchange-correlation functional[20] was used with the projector augmented wave (PAW) method.[21,22] Plane-wave basis sets were used with a cutoff energy of 1000 eV for the electron density and 1600 eV for the PAW augmentation charge. Standard VASP potentials were used for Al, B, and H. For Ca and Li semicore *s* and *p* states were included in the valence density. All atomic positions and the unit cell shape and volume were optimized to minimize the forces on the nuclei and the stress on the unit cell. Γ-centered *k*-space grids and the plane wave basis set cutoff energies were selected to converge the total energy of each system to better than 1 meV per conventional crystallographic unit cell. Initial crystal structures were taken from Weidenthaler *et al.*[7] for $Ca(AlH_4)_2$ and $CaAlH_5$, from Wyckoff[23] for CaH_2, and from Schmitt *et al.*[24] for CaB_6.

Harmonic phonon densities of states $g(\omega)$ were calculated by the direct method[17] as implemented in PHONON.[25] In this implementation the second derivatives required to construct the dynamical matrices are determined by finite differencing from force calculations. Two-sided differences were used in the calculations described here. Typical atomic displacements used were in the range 0.05–0.10 Å. Conventional crystallographic unit cells were used in the phonon calculations for $Ca(AlH_4)_2$ and $CaAlH_5$. $2\times2\times2$ supercells were used for CaH_2 and CaB_6.

From the frequency-dependent harmonic phonon density of states $g(\omega)$ the vibrational ZPE can be calculated, per unit cell, as

$$E_{ZPE} = \frac{\hbar r}{2}\int_0^\infty \omega g(\omega) d\omega, \quad (5)$$

where $\hbar$ is Planck's constant divided by 2π and r is the number of degrees of freedom in the unit cell. Similar integrals over $g(\omega)$ could be used to evaluate the vibrational free energy and the entropy.[26] In this work the ZPE was evaluated at the lattice parameters that minimized the potential energy. No attempt was made to include the effect of vibrations on the equilibrium geometry (for example, by applying the quasiharmonic approximation), which has been shown to have a negligible effect on the dehydrogenation enthalpy for a closely related system.[9]

III. RESULTS AND DISCUSSION

In previous work the crystal structure of $CaAlH_5$ has been given in the nonstandard space group $P2_1/n$.[7] To be compatible with PHONON, this crystal structure was transformed into the standard space group $P2_1/c$ using standard methods.[27] The resulting $P2_1/c$ representation of the $CaAlH_5$ structure was reoptimized. The resulting crystallographic data for $CaAlH_5$ in the $P2_1/c$ space group is given in Table I and the crystal structure is shown in Figs. 1(a) and 1(b). The crystal structures of $Ca(AlH_4)_2$ is shown in Fig. 1(c).

The optimized CaB_6 structure was similar to the experimentally determined $Pm\bar{3}m$ structure, with a=4.1469 Å and

TABLE I. Relative internal coordinates of atoms of the standard crystallographic space group $P2_i/c$ of $CaAlH_5$. The lattice parameters are $a=8.3247$ Å, $b=6.9665$ Å, $c=12.3668$ Å, and $\beta=127.938°$.

Atom	Site	Atomic coordinates
Ca	4*e*	(0.7737, 0.7703, 0.0419)
Ca	4*e*	(0.3313, 0.7293, 0.1451)
Al	4*e*	(0.8015, 0.6946, 0.3105)
Al	4*e*	(0.2097, 0.7840, 0.3400)
H	4*e*	(0.9487, 0.8096, 0.2757)
H	4*e*	(0.6063, 0.7150, 0.1393)
H	4*e*	(0.1051, 0.6493, 0.1948)
H	4*e*	(0.2652, 0.6014, 0.4511)
H	4*e*	(0.4350, 0.7866, 0.3665)
H	4*e*	(0.0088, 0.3072, 0.5176)
H	4*e*	(0.6970, 0.8891, 0.3402)
H	4*e*	(0.2637, 0.9452, 0.4615)
H	4*e*	(0.1189, 0.9758, 0.2143)
H	4*e*	(0.3544, 0.4351, 0.6642)

the boron atoms in 6*f* positions with $x=0.2017$. All other structures used in this work have been published previously.[7,9]

Figure 2 shows the calculated phonon density of states for $Ca(AlH_4)_2$, $CaAlH_5$, CaB_6, and CaH_2. The phonon density of states of $Ca(AlH_4)_2$ exhibited similar features to densities of states calculated for other similar complex metal hydrides.[8,10,28] Specifically, the density of states could be separated into three clearly identifiable groups of modes. The states contributing to the density at high frequencies corresponded to Al–H stretching motion. The group of modes in the medium frequency region were comprised primarily of AlH_4 bending modes. Low frequency modes involved relative motion of Ca ions and AlH_4 units.

In contrast to $Ca(AlH_4)_2$, in the $CaAlH_5$ structure [Fig. 1(a)] the aluminium and hydrogen do not exist in the distinct molecular ions common in complex metal hydrides. Instead, the structure comprises helical chains of corner sharing octahedra [Fig. 1(b)]. This strongly affects the phonon density of states. Within the helical Al/H structures, vibrational modes comprised primarily of Al–H stretches that include the hydrogen atoms shared between octahedra cannot exist. Any such vibrations that include Al–H stretches involving the corner-shared hydrogen atoms must also include a significant AlH_6 bending component. Likewise, any modes that include motion of the Ca cations relative to the Al/H helices that include any local Al–H motion (that is, are not whole helix translations) must be strongly coupled to Al–H stretching and AlH_6 bending modes. Thus the phonons in the three groups of modes are no longer distinguishable for this structure. The phonon density of states does not exhibit the large band gaps common in other complex metal hydrides, such as that shown in Fig. 2(a). Instead, the phonon spectrum exhibits an appreciable density of states across its entire range [Fig. 2(b)].

From the calculated phonon density of states, the ZPE per unit cell was calculated via Eq. (5) for all the calcium-containing phases in reactions (1)–(4) [$Ca(AlH_4)_2$, $CaAlH_5$, CaH_2, and CaB_6]. These are shown in Table II. ZPE for $LiBH_4$ and Al have been published previously.[9,29] For H_2 the ZPE was calculated in the harmonic approximation with vibrational frequency 4401 cm^{-1}.

Table III shows the calculated enthalpy changes for the dehydrogenation reactions (1)–(4). In all cases the inclusion of ZPE reduced the calculated enthalpy change the on dehydrogenation appreciably. For the "elementary" steps [that is, excluding the overall reaction (3)], the magnitudes of the reductions were of the order that has come to be expected.[8]

Without ZPE, our calculated enthalpy changes are in accord with those published by Alapati *et al.*[16] for reactions (3) and (4). The small discrepancies are easily accounted for as differences in details such as energy and geometry optimization convergence thresholds. Alapati *et al.* also published a

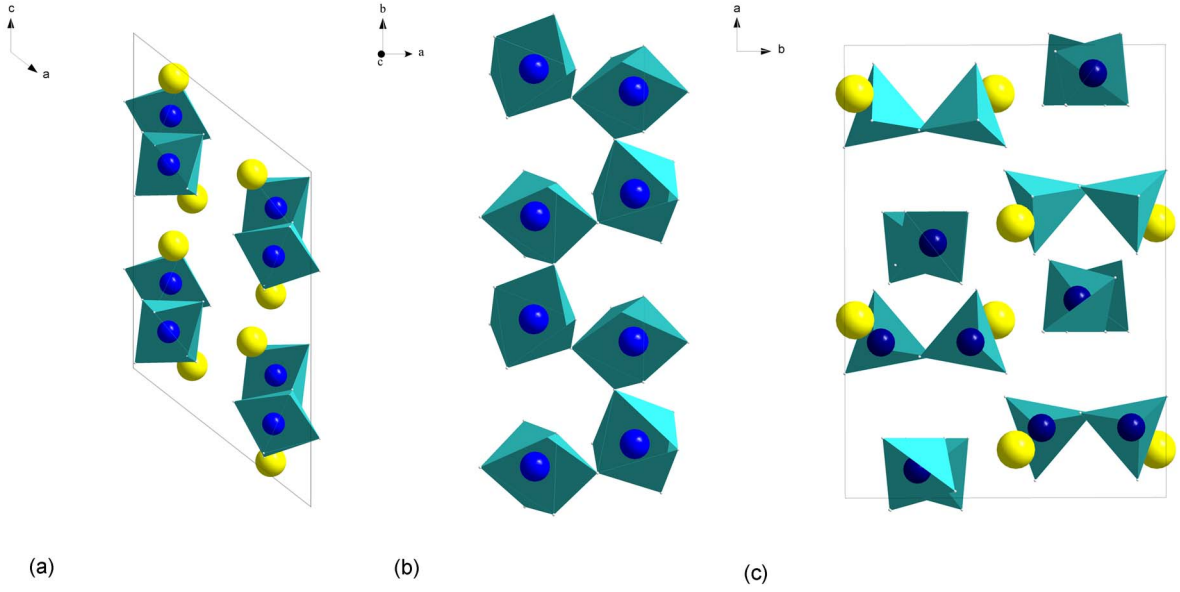

FIG. 1. (Color online) (a) The crystal structure of $CaAlH_5$ viewed down the *b* axis. (b) The helical arrangement of corner sharing [AlH_6] octahedra in $CaAlH_5$. (c) The crystal structure of $Ca(AlH_4)_2$.

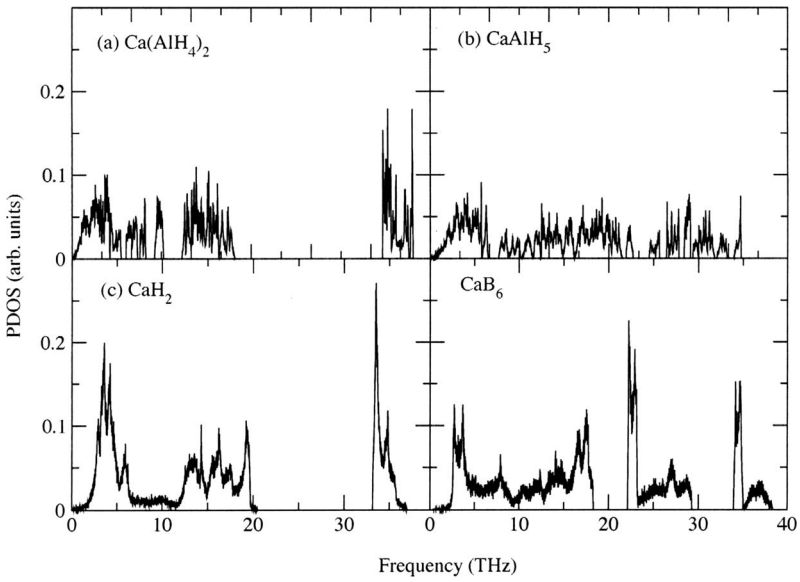

FIG. 2. Phonon density of states for (a) $Ca(AlH_4)_2$, (b) $CaAlH_5$, (c) CaH_2, and (d) CaB_6.

ZPE-corrected enthalpy change for reaction (4), which likewise agrees closely with our calculated value, differing by less than 1 kJ/mol H_2. This calculated dehydrogenation enthalpy, including ZPE effects, lies within the target range for hydrogen storage systems. Clearly, this is not a novel or particularly significant result, being previously reported. However, this represents an important independent validation of a representative example of the extensive calculations reported by Alapati *et al.*

Using a somewhat different treatment of vibrational effects, Wolverton and Ozoliņš calculated ZPE corrected enthalpy changes for reactions (1) and (2), and hence, by extension, reaction (3).[14] For reaction (1) the two sets of energies and enthalpies are similar. Both the calculated potential energy differences and the calculated ZPE differences are close.

For reaction (2) there is more of a discrepancy. Although the ZPE corrected enthalpy calculated here was 6 kJ/mol H_2 larger than the previously published value, this cannot be ascribed to the different treatment of phonons alone. The calculated potential energy difference was even larger, with the value calculated in the current work more than 10 kJ/mol H_2 larger than the previously published value. Thus it appears that the smaller difference between the two calculated enthalpy change values relies to some extent on a cancellation of errors in one or both of the calculations. Unfortunately this means that we can draw no direct conclusions about the two phonon analysis method in this case, as the underlying potential surfaces being probed by the phonon analysis appear to be significantly different.

TABLE II. Calculated potential energy (as calculated by VASP, relative to spherically symmetric, isolated reference atoms) and ZPE for calcium-containing phases calculated in this work (eV/formula unit).

	Potential energy	ZPE
$Ca(AlH_4)_2$	−38.6758	1.5776
$CaAlH_5$	−24.8555	1.0231
CaH_2	−10.3251	0.2919
CaB_6	−45.0062	0.7863

It has been shown[3,5] that the dehydrogenation represented in reaction (3) is the sum of two steps, reactions (1) and (2). With or without ZPE contributions, the first step of the decomposition of calcium alanate was calculated to be significantly exothermic, and thus uninteresting from the point of view of hydrogen storage.[7,14] The second step, itself accounting for a storage capacity of 4.2 wt %, has a potential energy change on dehydrogenation that does lie within the desired enthalpy change range for a hydrogen storage material.[7] However, adding contributions from ZPE reduces this calculated enthalpy change to significantly below the 30 kJ/mol H_2 lower limit[1] of the target enthalpy change range.

In their screening of destabilized hydride storage systems, Alapati *et al.*[16] considered separately systems that involved combining $Ca(AlH_4)_2$ with another complex metal hydride, on the basis that the decomposition of $Ca(AlH_4)_2$, with its low reaction enthalpy, was likely to compete with the destabilized path. The dehydrogenation enthalpy for $CaAlH_5$ is also below the lower limit for hydrogen storage systems and is thus in principle subject to the same considerations as $Ca(AlH_4)_2$ from the point of view of "short-circuiting" destabilization schemes. That is, destabilized mixed hydride storage schemes that contain a $CaAlH_5$ phase and yield a dehydrogenation enthalpy in the target range must rely on kinetic hindrance of the $CaAlH_5$ decomposition path. Otherwise attractive destabilization schemes involving $CaAlH_5$ are likely to be at best metastable.

Note also that destabilization schemes involving Ca and Al should be designed with the $CaAlH_5$ intermediate in mind, rather than the more traditional alanate $Ca(AlH_4)_2$. In particular, rehydrogenation of a calcium- and aluminium-containing system would be expected to stop at $CaAlH_5$ rather than continuing to $Ca(AlH_4)_2$ via the endothermic reverse of reaction (1).

TABLE III. Low temperature and pressure enthalpy changes for dehydrogenation reactions (kJ/mol H_2).

Reaction	ΔH without ZPE	ΔH with ZPE	$-\Delta(\Delta H)$	Other results
$Ca(AlH_4)_2 \rightarrow CaAlH_5+Al+3/2H_2$	−5.3	−12.3	7.0	−12.9[a]
$CaAlH_5 \rightarrow CaH_2+Al+3/2H_2$	40.3	22.0	18.4	15.9[a]
$Ca(AlH_4)_2 \rightarrow CaH_2+2Al+3H_2$	17.5	4.8	12.7	1.5[a]
$CaH_2+6LiBH_4 \rightarrow CaB_6+6LiH+10H_2$	60.2	40.7	19.5	42.4[b]

[a]The reaction enthalpies ΔH (kJ/mol H_2) include the ZPE calculated using the frozen-phonon method (Ref. 14).
[b]The reaction enthalpies ΔH (kJ/mol H_2) include the ZPE calculated using the direct method (Ref. 16).

IV. CONCLUSIONS

We have performed DFT calculations at the generalized gradient approximation level for the dehydrogenation reactions of $Ca(AlH_4)_2$, $CaAlH_5$, and $CaH_2+6LiBH_4$. Harmonic phonon ZPE was included. $Ca(AlH_4)_2$ was confirmed to be a metastable hydride, and thus unsuitable as a medium for a cyclable hydrogen storage system. $CaAlH_5$ is stable, but calculations including ZPE effects indicate that it is not stable enough for a hydrogen storage system operating near ambient conditions. ZPE-corrected enthalpy calculations confirm the destabilized combination of $LiBH_4$ with CaH_2 is a promising system, as previously reported. As far as could be consistently tested in this work, ZPE differences calculated by the direct method phonon analysis that is gaining popularity and by the older frozen-phonon approach were found to be consistent.

ACKNOWLEDGMENTS

The work presented here has been supported by an NWO grant under the ACTS Hydrogen program. We would like to thank Geert-Jan Kroes for useful discussions.

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