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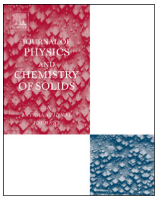

First-principles study of structural stabilities of AlH_3 under high pressure

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ABSTRACT

The structural stabilities and electronic properties of AlH_3 under high pressure are investigated by using the plane-wave pseudopotential method. Our results demonstrate that the sequence of the pressure-induced phase transition is $Fd\bar{3}m(\beta)\rightarrow cmcm(\alpha')\rightarrow R\bar{3}c(\alpha)\rightarrow Pnma(hp1)\rightarrow Pm\bar{3}n(hp2)$, and the transition pressures are 0.49, 0.91, 47, and 70 GPa, respectively. $Im\bar{3}m$, $Pnnm(\gamma)$ and $P63/m$ structures are not stable in the 0–100 GPa. β, α', α, and $hp1$ structures of AlH_3 are nonmetals, while $Pm\bar{3}n$ structure of AlH_3 is metallic, and the pressure-induced metallization is ascribed to phase transition under higher compression.

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1. Introduction

Aluminum trihydride (AlH_3) is a very important material because it is one of the byproducts in most of the dehydriding reactions in Al based hydrides. AlH_3 has application as an energetic component in rocket propellants and a reducing agent in alkali batteries and polymerization catalysts. Moreover, it is a unique binary hydride having at least seven crystalline phases with different physical properties and with the largest hydrogen content of 10.1% by weight [1]. Its gravimetric hydrogen density is two times higher than liquid hydrogen and much higher than that of most of the known metal hydrides. Moreover, Al is a commonly available and recyclable material. Thus, AlH_3 is considered as a possible hydrogen storage material [2].

AlH_3 had been studied both experimentally [3–6] and theoretically [1,7,8] due to its potential applications as storing hydrogen. Moreover, almost all these studies focused on the determination of the pressure-induced phase transition. To our knowledge, eight different crystalline forms of AlH_3 have been reported under different pressures, such as β, α', α, $hp1$, γ, $Pm\bar{3}n$, $P63/m$, and $Im\bar{3}m$ [1,3,5–7]. Synchrotron X-ray diffraction studies reveal that β-AlH_3 is the ground-state structure, and transforms into α phase up to 6 GPa. Raman scattering study at high pressure for both β- and γ-AlH_3 exhibits transition into the α phase with high concentration of structural defects [6]. Under further compression, other several high-pressure phases (with space group $Pnnm$, $P63/m$, $Pm\bar{3}n$, and $Im\bar{3}m$) were proposed by theoretical calculations [1,5]. Pickard and Needs predicted a transition from low-pressure α phase to an insulating layered $hp1$ phase at 34 GPa, and further a transition to a semimetallic $hp2$ phase at 73 GPa by a density functional theory method and a random searching technique [7]. Vajeeston et al. investigated the structural stabilities by density-functional total-energy calculations, and application of pressure makes the sequence of phase transitions from $\beta\rightarrow\alpha'\rightarrow\alpha\rightarrow P63/m\rightarrow hp2$ and the estimated transition pressures are 2.4,4.3, 64, and 104 GPa [1]. However, no first-order structural transitions were observed up to 7 GPa for AlH_3 by using synchrotron X-ray powder diffraction studies [9], which is consistent with earlier high pressure studies [10,11]. The pressure dependence on the electronic structure is also discussed by first-principles density-functional-theory calculations [1,9]. Owing to the difficulties in determining accurately the hydrogen positions in a metal matrix by X-ray diffraction measurements, several critical issues for the phase transition sequence of AlH_3 under compression are still under debate in experimental studies. Accordingly, much more experimental and theoretical efforts are needed to understand the high pressure behaviors of AlH_3. These provide us with the motivation to undertake a detailed investigation of phase transition for AlH_3, and to analyze the difference of electronic properties for the eight different crystalline forms, by employing the plane-wave pseudopotential method based on density functional theory. The rest of paper is organized as follows. In Section 2, we briefly describe the computational details used in the present work. Results and discussion will be presented in Section 3. A summary of the work will be given in Section 4.

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Table 1
Summary of calculated lattice constants, atomic fractional coordinates, bulk modulus B and its pressure derivative B' at zero pressure for eight possible candidate structures of AlH_3, available previous experimental and theoretical data with brackets are included for comparison.

Structure (space group)	Lattice constants (Å)	Atomic positional parameters	B (GPa)	B'
β	a=9.0494[9.0037[a],9.065[b]]	Al(0.5,0,0),H(0.4310,1/8,1/8)	36[34[b]]	2.8[2.5[b]]
α'	a=6.508[6.470[a],6.523[b]]	Al1(0,0.5,0),Al2(0.25,0.25,0)	35[27[b]]	3.4[4.5[b]]
	b=11.112[11.117[a],11.139[b]]	H1(0,0.2145,0.4443),H2(0.3098,0.1025,0.0501)		
	c=6.583[6.562[a],6.604[b]]	H3(0,0.4566,1/4),H4(0.2934,0.2857,1/4)		
α	a=4.460[4.449[c],4.492[b]]	Al(0,0,0)	34[28[b]]	4.2[5.4[b]]
	c=11.770[11.804[c],11.821[b]]	H(0.628,0,1/4)		
hp1	a=4.428[4.432[d]]	Al(0.1152,1/4,0.5548)	45	4.5
	b=6.488[6.500[d]]	H1(0.3391,0.424,0.8103)		
	c=4.083[4.089[d]]	H2(0.4371,1/4,0.3202)		
hp2	a=3.590	Al(0,0,0),H(1/4,0,1/2)	106[39[b]]	3.8[6.2[b]]
P63/m	a=5.416[5.385[b]]	Al(2/3,1/3,1/4)	[43[b]]	[8.1[b]]
	c=2.478[2.484[b]]	H(0.5897,0.6980,1/4)		
γ	a=5.429[5.381[e],5.456[b]]	Al1(0,0,0.5),Al2(0.7885,0.0851,0)	[42[b]]	[2.1[b]]
	b=7.408[7.356[e],7.404[b]]	H1(0,0.5,0.5),H2(0.672,0.2992,0)		
	c=5.788[5.775[e],5.801[b]]	H3(0.098,0.1385,0),H4(0.799,0.0818,0.2974)		
$Im\bar{3}m$	a=3.809	Al(0,0,0),H(1/2,0,0)		

[a] Ref. [18]
[b] Ref. [1]
[c] Ref. [19]
[d] Ref. [7]
[e] Ref. [20]

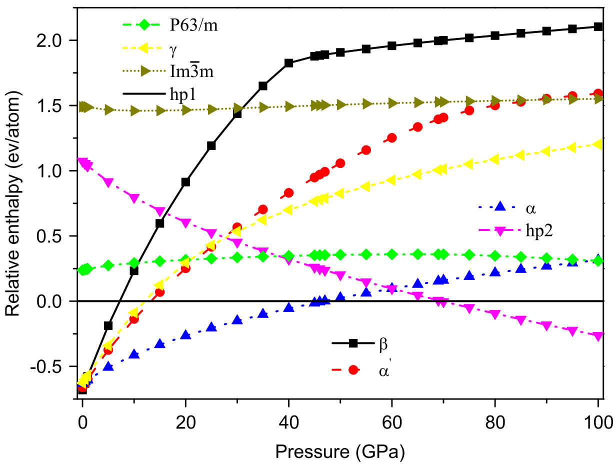

Fig. 1. Calculated enthalpy differences of all these actual and possible structures of AlH_3 with respect to *hp1* phase as a function of pressure.

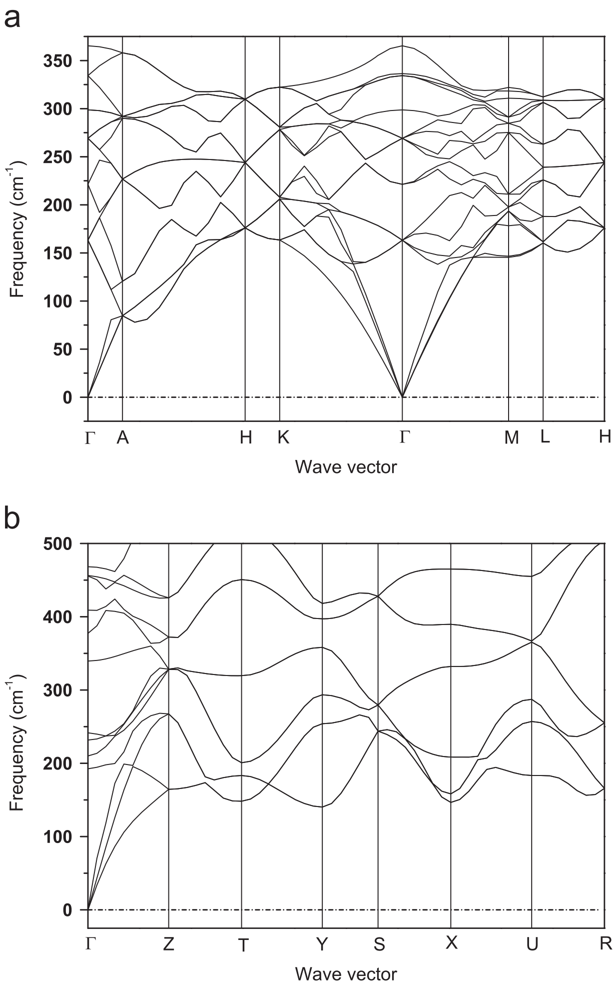

Fig. 2. Calculated phonon dispersion curve for (a) α and (b) *hp1* structure of AlH_3 at the transition pressure.

2. Computational details

Our calculations were performed using the plane-wave pseudopotential method as implemented in the CASTEP code [12]. The electronic exchange–correlation interactions are treated within the generalized gradient approximation (GGA-PBE) of Perdew et al. [13]. The norm-conserving pseudopotentials were employed to model the ion–electron interactions [14]. The energy cutoff of the plane-wave basis was chosen as 900 eV. The special points sampling integration over the Brillouin zone was employed by using the Monkhorst–Pack method with k-points separation of 0.025/Å for all possible polymorphs of AlH_3 [15]. The chosen plane-wave cutoff and the number of k points were carefully checked to ensure the total energy converged to better than 1 meV/atom. The tolerance for geometry optimization was difference on total energy within 5×10^{-6} eV/atom, maximum ionic Hellmann–Feynman force within 0.01 eV/Å, maximum ionic displacement within 5×10^{-4} Å, and maximum stress within 0.02 GPa. For a given external hydrostatic pressure, lattice constants and internal coordinates of atoms are fully relaxed. The phonon frequencies were calculated based on the density functional linear-response method [16].

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