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**Low-pressure Structural Modification
of Aluminum Hydride**

by Jennifer A. Ciezak-Jenkins

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<p>In-situ isothermal high-pressure synchrotron x-ray diffraction and optical Raman spectroscopy were used to examine the structural properties, equation of state, and vibrational dynamics of alpha-aluminum hydride (AlH₃). The x-ray measurements show that the pressure-volume relations remain smooth to near 50 GPa. Although there is no evidence for a first-order phase transition, the unit cell axial ratio (c/a) is anomalous near 2.5 GPa, which correspond to the onset of a monoclinic structural distortion. Infrared measurements conducted within a similar pressure range show a distinct discontinuity in the frequencies of the Al-H lattice modes. The combined data provide evidence for a monoclinic structural distortion beginning near 2.5 GPa. The results are consistent with recent synchrotron x-ray diffraction measurements and theoretical calculations. All structural changes are reversible upon pressure release.</p>					
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1. Introduction

Since its synthesis was first reported in the 1950s (1), the physical and chemical properties of aluminum hydride (AlH_3) have been assessed for a number of applications, ranging from hydrogen storage to rocket propulsion. Although early thermodynamic calculations suggested the material would be an ideal propellant, the stability and sensitivity issues of the material could not be overcome until the development of a new synthesis process by SRI International in the late 90s (2). The SRI synthesis method considerably improved the purity of the yield of the most thermodynamically stable polymorph, α -aluminum hydride, and subsequent analysis in solid propellant applications conducted by the Navy at China Lake suggested significant improvements in propulsion properties over the material synthesized in earlier attempts (3). Computational simulations have predicted that replacement of aluminum (Al) with AlH_3 would result in a 10% gain in specific impulse for over 20 s; such an improvement over Al propellants is possible because of the low ignition (1450 K) and combustion (3391 K) temperatures of AlH_3 (4, 5). However, its widespread implementation into propellant formulations has been complicated by reproducibility in performance characteristics from seemingly similar synthesis conditions, as well as its sensitivity towards oxidation, hydration, and friction, although some progress has been made in the stabilization by using a coating or additives (6).

Six polymorphs of AlH_3 have been identified (7), four of which have been reproducibly synthesized with well-characterized crystal structures (8–11), with the α -phase being the thermodynamically stable form at ambient conditions. As is shown in figure 1, α -aluminum hydride has AlH_6 octahedrons linked by Al-H-Al bridges arranged in a rhombohedral lattice. The crystal structure of the α -aluminum hydride has been examined by x-ray diffraction up to pressures of 160 GPa (12–14) and by neutron diffraction to 7.2 GPa (15). Although several x-ray studies as well as the neutron diffraction have shown the rhombohedral lattice structure persists to pressures approaching 75 GPa (14), Graetz et al. (13) suggested a monoclinic distortion of the rhombohedral unit cell occurs under very modest pressures between 1 and 7 GPa, as a result of the tilting of the AlH_6 octahedral units and shrinking of the Al-H bond distance. Since subsequent high-pressure x-ray diffraction and Raman spectroscopic (16, 17) studies have not observed convincing evidence of the monoclinic distortion, considerable ambiguity exists as to the exact phase behavior of AlH_3 at pressures below 10 GPa. It is well known that crystal structure and bonding strongly influence the physical and chemical characteristics of a material—diamond, for example, has considerably different properties than graphite, and conclusive evidence regarding the monoclinic distortion may help to explain the discrepancies in performance between two batches synthesized under seemingly similar conditions. As such, the phase behavior of AlH_3 under moderate pressure conditions warrants further examination.

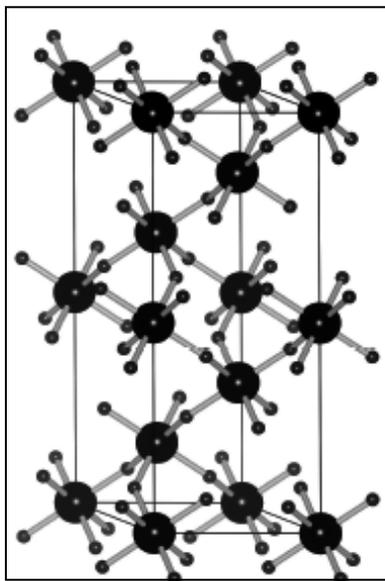


Figure 1. The crystal structure of α -AlH₃. The larger and smaller atoms correspond to Al and hydrogen, respectively. Reproduced from reference 17.

2. Experimental Methodology

Aluminum hydride was obtained from ATK Thiokol and used without further purification; the sample was stored in a dry atmosphere between experimental runs. A flake of approximately 50 microns in diameter and a thickness of 20 microns was positioned in a piston-cylinder type diamond anvil cell equipped with 300-micron diamond culets and a stainless steel gasket. For both the infrared (IR) spectroscopic and x-ray diffraction measurements, a neon pressure medium was loaded into the diamond anvil cell using a specialized high-pressure gas loading system (18). The in-situ pressure within the diamond anvil cell was determined from the frequency shift of the ruby R₁ luminescence of a micrometer-sized ruby sphere (19).

Room temperature isothermal angle dispersive x-ray powder microdiffraction experiments were conducted at Beamline 12.2.2 of the Advanced Light Source by using focused monochromatic x-rays ($\lambda = 0.4959 \text{ \AA}$) and a high-resolution image plate detector. The recorded two-dimensional diffraction images were then integrated to produce high-quality angle dispersive x-ray diffraction patterns using FIT2D. Synchrotron IR absorption measurements to near 20 GPa were obtained at beamline U2A of the National Synchrotron Light Source (NSLS) of Brookhaven National Laboratory (BNL). The spectral resolution of $\pm 4 \text{ cm}^{-1}$ was used for all IR measurements.

3. Results and Discussion

3.1 X-ray Diffraction

The alpha phase of AlH_3 has a rhombohedral lattice of space group $R\bar{3}c$ (8) and consists of structures built from AlH_6 octahedrons linked by Al-H-Al bridges. The lattice parameters for the rhombohedral cell are $a = 4.492 \text{ \AA}$ and $c = 11.821 \text{ \AA}$ at 0.0 GPa and 295 K (8). Good agreement with previously reported results (14) for the rhombohedral unit cell was observed with eight characteristic diffraction peaks below 25° at 0.3 GPa, as is shown in figure 2. To better understand the phase behavior of α -aluminum hydride subjected to moderate pressures, x-ray diffraction was measured upon isothermal compression at room temperature to pressures near 50 GPa. The diffraction peaks identified at near ambient conditions remain traceable over the entire pressure range studied and no new reflections are noted that could signify a phase transition. A generalized loss of diffraction intensity is observed, which may be attributed to thinning of the sample in response to compression. Additionally, broadening of the diffraction peaks are noted, which was previously used to support the proposed monoclinic distortion. Although conclusive evidence cannot be drawn from the x-ray diffraction results of this study alone, when coupled with the detailed analysis of the infrared spectroscopic trends discussed below, the broadening does appear to support the distortion.

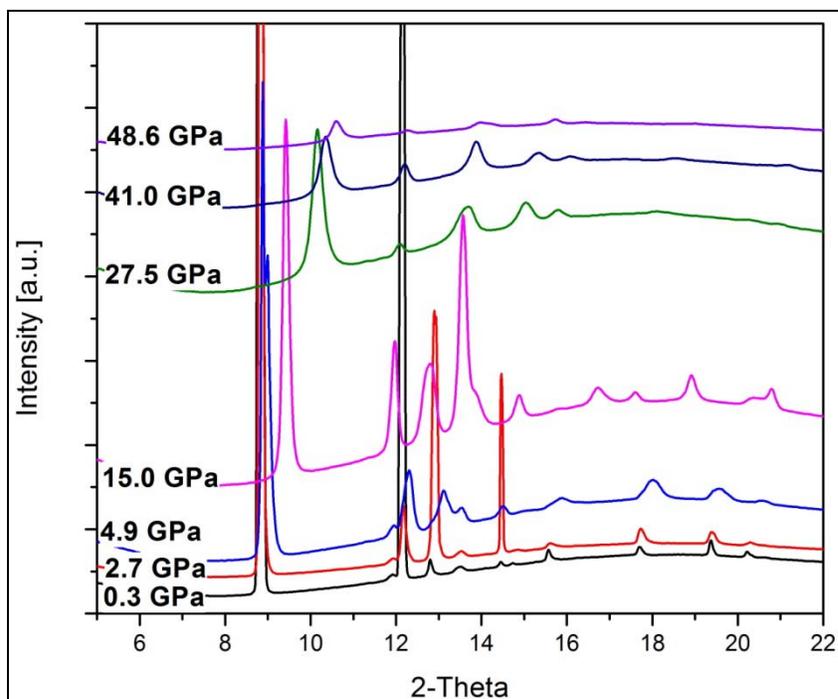


Figure 2. Select in-situ x-ray diffraction patterns of AlH_3 measured upon isothermal compression at ambient temperature. The diffraction patterns are offset for clarity.

The lattice parameters a and c for a rhombohedral cell in a hexagonal framework give the pressure dependence of the axial ratio, c/a , for the unit cell, also referred to as the deformation parameter. The results are shown in figure 3. There is a distinct discontinuity near 2.3 GPa, which may reflect the onset of the monoclinic structural modification. Figure 4 shows the pressure-volume (P-V) equation of state (EOS) data determined from the diffraction data fit to the rhombohedral unit cell, coupled with the results of an earlier high-pressure experiment (14). The experimental data from this study was fit using a third-order Birch-Murnaghan EOS (20). No sharp discontinuities, which could indicate a phase transition, are observed in the EOS data obtained from this study. A bulk modulus of $K_0 = 45.3 \pm 0.4$ GPa and a pressure derivative $K_0' = 3.6 \pm 0.5$ GPa was derived from the fit. These values are slightly larger than the previous values of $K_0 = 42.3$ GPa and $K_0' = 3.5$ reported by Goncharenko et al. (14), but well within the error limits. The lack of discontinuities in the EOS at low pressures suggests the monoclinic distortion to the rhombohedral unit cell is very subtle.

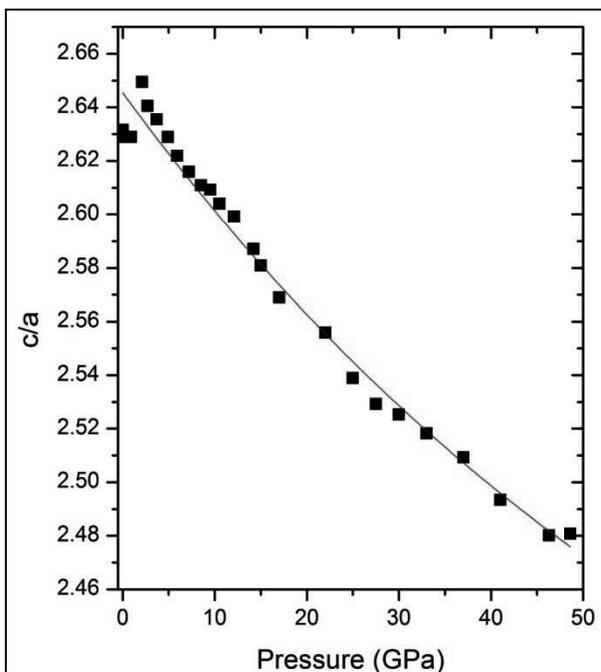


Figure 3. Variation for the c/a ratio with pressure. The solid line is drawn to guide the eye.

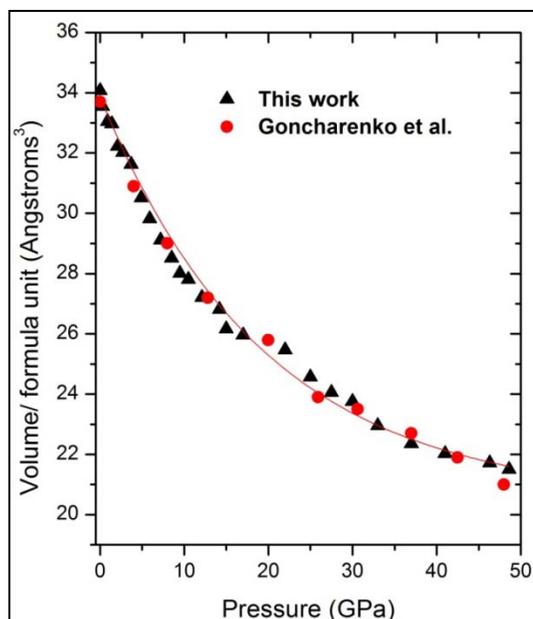


Figure 4. Volume per formula unit of AlH_3 as a function of pressure from this study (triangles). The red line is a fit of the experimental data using a third-order Birch Murnaghan equation (20). Circles indicate the high-pressure data of Goncharenko et al. (14).

3.2 Infrared Spectroscopy

Select IR spectra of AlH_3 on isothermal compression at room temperature up to 25 GPa are shown in figure 5. The frequencies of the vibrational bands are plotted as a function of pressure in figure 6. All of the fundamental vibrations were identified by Roszinski et al. (21) and Kolesnikov et al. (22). AlH_3 has six IR active modes ($2A_u + 4E_u$), but the spectral resolution permitted only identification of four IR-active bands: Al-H bending modes near 650 and 850 cm^{-1} and Al-H asymmetric stretching modes near 1665 and 1775 cm^{-1} . At pressures below 2.7 GPa, a weak band is observed near 2200 cm^{-1} , which can be attributed to the diamond anvils.

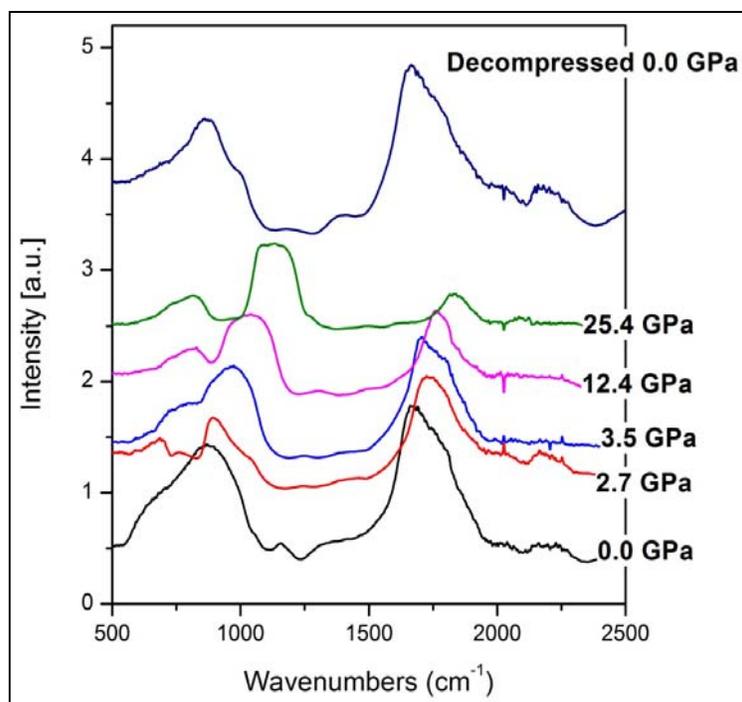


Figure 5. IR spectra of AlH₃ as a function of pressure in the spectral range between 500 and 2500 cm⁻¹. Spectra are offset for clarity.

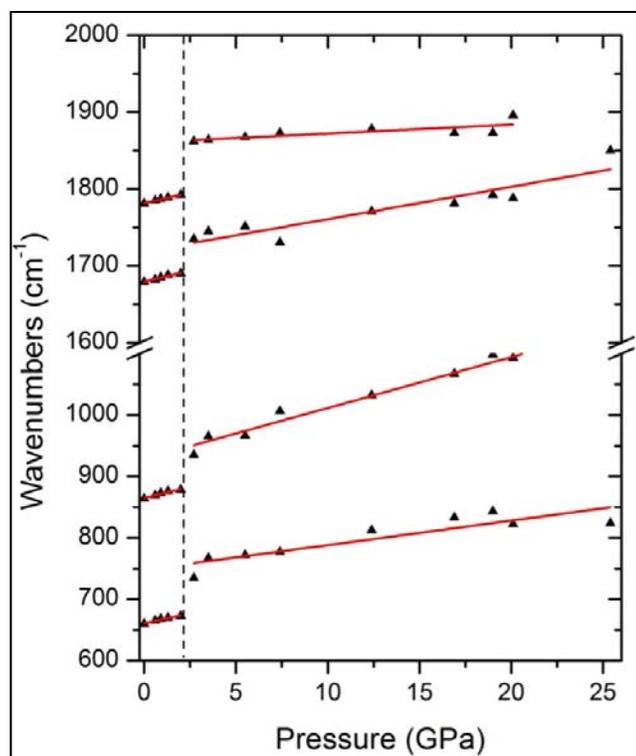


Figure 6. Pressure dependence of the frequencies of the four observed IR active modes. The dashed line indicates the onset of the structural discontinuity. Linear fits are shown for the frequency shifts.

The following are immediately noticeable in the spectra over the pressure range studied:

1. The spectral intensities of the 1665 cm^{-1} and its shoulder vibration at 1775 cm^{-1} diminish gradually with increasing pressure. Near 25 GPa, the broad doublet splits into two well-defined bands.
2. At ambient pressure, the 650 and 850 cm^{-1} Al-H bending modes appear as a single broad band with a well-resolved shoulder. Slightly above 2.5 GPa, the band splits into two distinct features due to an abrupt shift in the frequencies of the two modes. The two modes persist as singlet bands to 25.4 GPa.
3. The 650 cm^{-1} band splits into a weak doublet near 12 GPa. It can be speculated that this splitting is the result of the Davydov effect, where the molecular symmetry of the unit cell is distorted resulting in slightly differing vibrational frequencies.
4. All spectroscopic changes are reversible upon pressure release.

As mentioned previously, slightly above 2.5 GPa, nonlinearities as a function of pressure are observed for the four IR-active vibrational modes. IR frequencies measured at 3 GPa and above do not extrapolate down to the ambient pressure values observed from the decompressed

recovered samples. A monoclinic phase distortion resulting from the increasing tilt of the AlH_6 octahedral units was proposed on the basis of high-resolution x-ray diffraction measurements between 1 and 7 GPa (13). The observation suggested that the transition may be second or higher order and result in a mixture of phases, as in iron titanium hydride (23).

4. Discussion and Conclusions

Goncharenko et al. (14) investigated the phase behavior of AlH_3 by x-ray diffraction to 160 GPa. The results confirmed the slight variation in the experimentally observed positions of the Bragg peaks from the calculated positions of the R-3c space group, which was earlier attributed to a monoclinic distortion of the alpha phase between 1 and 7 GPa (13). In both studies, the structural deviation was attributed to slight pressure gradients within the diamond anvil cell. The pressure dependence of the volume derived from this study was plotted and compared to the Goncharenko et al. (14) study with good agreement between the two within experimental error. However, it is interesting to point out the c/a ratio derived from the x-ray diffraction in the current experiments has a distinct discontinuity near 2.7 GPa, which coincides with a similar discontinuity in the IR frequencies near this pressure. While the origin of this phenomenon remains speculative, several independent x-ray diffraction patterns obtained near this pressure also demonstrated the discontinuity.

The combined high-pressure IR and x-ray results suggest that the monoclinic distortion occurs sluggishly near 2.5 GPa, but the distortion does not result in a complete phase transition over the entire pressure range studied. Under increasing pressures at room temperatures, displacements and the dipole-dipole interactions between the neighboring AlH_6 octahedral units occur. The Al-H bending modes involves the relative displacement of the octahedral units along the a lattice vector. Initially, the hydrogen is symmetrically located between two neighboring AlH_6 octahedra at a distance of 1.703 Å (13), but upon compression over the threshold value of 2.5 GPa, destabilization of the octahedral units occurs as a result of the shrinking Al-H bond. Further, the large split of the Al-H bending modes suggests the effect is not symmetric across the cell. Given that this effect was reproduced in several independent experiments, it seems highly unlikely that deviatoric stresses from pressure media could be the cause. The origin of the monoclinic distortion will be examined in future work using high-pressure radial diffraction techniques.

The present study has provided new information on the monoclinic distortion of the rhombohedral unit cell of AlH_3 . As was previously observed, the alpha phase has a large region of thermodynamic stability at ambient pressure persisting to near 60 GPa (14). Under relatively modest pressures, structural changes were documented between 2 and 4 GPa by x-ray diffraction and IR spectroscopy. On compression at room temperature, an abrupt frequency discontinuity is observed in the Al-H bending and Al-H stretching modes, which implies a structural transformation. Concordant with the IR results, the pressure dependence of the c/a axial ratio

anomalous near 2.7 GPa. All changes observed upon compression are fully reversible. Further experiments are underway to determine the cause of the structural instability.

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List of Symbols, Abbreviations, and Acronyms

Al	aluminum
AlH ₃	aluminum hydride
BNL	Brookhaven National Laboratory
EOS	equation of state
IR	infrared
NSLS	National Synchrotron Light Source
P-V	pressure-volume

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