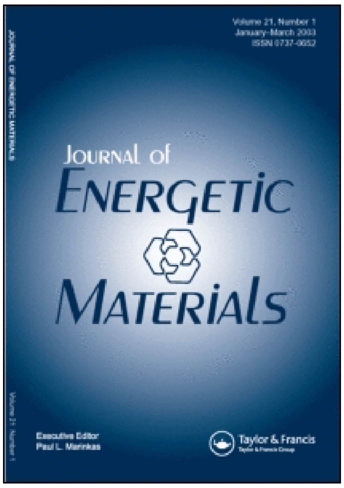

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Chak-pan Wong[a]; Philip J. Miller[a]
[a] Indian Head Division, Naval Surface Warfare Center, Indian Head, Maryland, USA

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Vibrational Spectroscopic Studies of Alane

CHAK-PAN WONG
PHILIP J. MILLER

Indian Head Division, Naval Surface Warfare Center,
Indian Head, Maryland, USA

Alane has been subjected to Raman studies under static compression. The Raman spectra showed four modes, which increased in frequency as pressure was increased from ambient to 6.6 GPa. From the pressure dependence, the pressure coefficient, $d\nu_i/dP$, for each mode has been estimated and used to evaluate the mode Grüneisen parameter γ_i for that mode. Independently the thermodynamic Grüneisen parameter γ_{th} has also been calculated using the pressure derivative of the isothermal bulk modulus value from the literature. Preliminary infrared spectra were also collected under ambient conditions and are discussed with those reported in the literature for alane polymorphs.

Keywords: Raman, infrared, alane, compression

Introduction

Aluminum trihydride, AlH_3, or alane, has been evaluated for solid propellant applications by Navy researchers at the Naval Air Warfare Center at China Lake [1]. It was concluded that it had potential for such applications, because it was possible to obtain good purity for the most stable polymorph [2], the α polymorph, and good morphology for propellant processing.

Address correspondence to C.-P. Wong, Indian Head Division, Naval Surface Warfare Center, Indian Head, MD 20640, USA. E-mail: chak.wong@navy.mil

The thermal stability of α-AlH_3 also seemed adequate for such applications. Since energetic materials are used at high-pressure conditions, we need to know their characteristics at high pressures. Vibrational spectroscopic studies would be useful in the study of phase transitions as pressure is increased. There have been very few vibrational spectroscopic studies for alane polymorphs, at ambient or nonambient conditions. In particular, no Raman studies have been reported in the open literature. Here we report the spectroscopic studies obtained with Raman and infrared spectroscopy of alane under both ambient conditions and static compression.

Under ambient conditions aluminum trihydride, AlH_3, exists as a polymerized solid, with both ionic and covalent characteristics, although it is more ionic and only partially covalent [3]. To reflect this polymeric characteristic, the formula of aluminum hydride is sometimes given as $(AlH_3)_n$ [4]. This compound can exist in several metastable polymorphs, the most stable of which is the alpha form [2]. This is the form that has been subjected to the Raman and IR studies reported here. A single alane molecule has the symmetry represented by the point group D_{3h} [5]. But the polymorph α-AlH_3 has a hexagonal unit cell with six molecules per cell and belongs to the space group $R\ \bar{3}c$ ($\equiv D^6_{3d}$) with $a = 4.449$ Å and $c = 11.804$ Å in hexagonal axes [4].

Background

A brief review of the literature relevant to our studies will now be given. Infrared spectra at ambient conditions have been reported in a U.S. patent by Dow Chemical Co. [6] for the α'-AlH_3 which is similar to the α form. German researchers [7] have also reported ambient IR spectra of $(AlH_3)_n$. Inelastic neutron scattering studies have been reported for α-AlH_3 at 25 K [8] from which a generalized vibrational density of states has been calculated. Theoretical calculations based on density functional theory have also been reported for α-AlH_3, and zone-center phonon energies were estimated [9]. These energies are experimentally measurable with Raman and infrared spectroscopy and will be compared with the Raman results obtained in our studies. From X-ray studies, compressive curves of α-AlH_3 at ambient temperature have been reported from ambient pressure to 5.4 GPa [10]. But higher pressure X-ray structural studies have also been reported [3]; in this work no phase transitions were observed, at room temperature, up to a maximum pressure of 35 GPa. Bulk modulus values were deduced in both studies (32.7 GPa and 47.9 GPa, respectively). The α-AlH_3 polymorph is structurally isomorphous to the α-AlF_3 polymorph of the aluminum trifluoride family, and Raman studies have been reported for the trifluoride [11]. The Raman spectra of these two compounds will be discussed.

Experimental Approach

The source material was studied with X-ray diffraction techniques and identified as the α-AlH_3 polymorph. Powder samples obtained from Russia and used in Raman spectroscopic studies were loaded in a sapphire anvil cell, the Merrill-Bassett cell. The material was contained in a hole drilled in a gasket and confined by the two sapphire anvils and the cylindrical wall of the hole. The gasket material was Inconel, an alloy of Ni, Cr, and Fe, chosen for its strength and anticorrosion properties. The gasket had a thickness of 127 µm, and the size of the hole was 150–250 µm depending on the size of anvils used. The amount of sample used was several hundred µg, estimated from the density and calculated volume of the gasket hole. Ruby spheres ~20–30 µm in size were put in the gasket hole on top of the sample for the pressure measurements described below. One was placed near the hole center and one off center. The actual sizes of the rubies were not measured.

Raman spectroscopic studies using the spectrometer in this study have been reported earlier [12]. Briefly, Raman spectra were collected with a Spex 1403 spectrometer of 0.85 m focal length with a band pass of about $5\,cm^{-1}$. Back-scattering geometry was used as shown in Figure 1. The 514.5 nm line from an argon ion laser with maximum total output of about 130 mW was used to excite the sample, and the scattered signal was detected with a liquid nitrogen–cooled CCD detector.

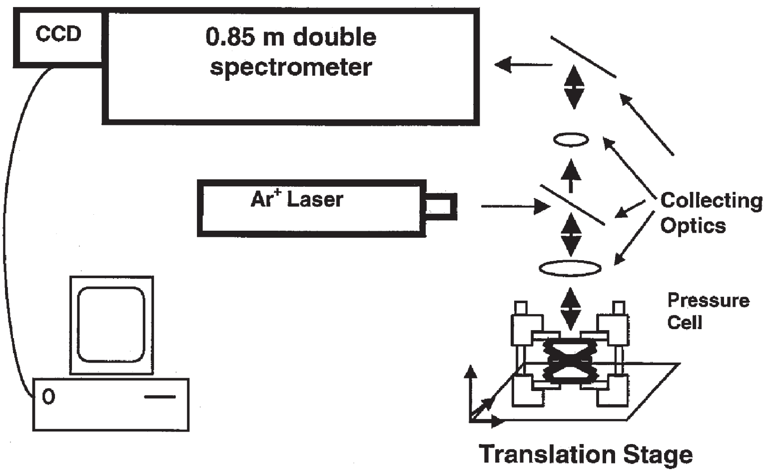

Figure 1. Raman spectrometer and pressure cell.

The laser light was split by a beam splitter, and part of the light was focused onto the sample contained in the pressure cell. The back-scattered light was collected and focused onto the entrance slit of the spectrometer. An optimal signal was obtained through adjustment of the translation stage. Neon and mercury emission lines from pen lamps were used for spectral calibration. Peak positions were determined by fitting a Gaussian function to the observed Raman modes by using Igor Pro software [13]. Attenuated total reflectance infrared spectroscopy was used to collect the IR spectra of alane under ambient conditions. A Nicolet spectrometer, model AVARAR 370, with a ZnSe crystal was used.

A ruby sphere placed approximately at the center was used to measure the static pressure applied to the sample. This method is based on the pressure dependence of the fluorescence wavelength when an argon ion laser at 514.5 nm wavelength excites the ruby. The incident power was reduced to less than 0.05 mW to prevent heating in the ruby. The positions of the ruby fluorescence lines R_1 and R_2 were measured for each pressure, and the pressure was calculated; R_1, R_2 wavelengths are 694.2 and 692.8 nm, respectively, under ambient conditions.

To focus the laser light onto a ruby, the sample in the gasket hole was first displayed in a monitor by means of a camera. Then the translation stage was adjusted until the ruby fluoresced in the red. Since no pressure-transmitting medium was used, the studies were conducted under nonhydrostatic conditions. A pressure gradient existed and was estimated from a ruby sphere placed at an off-center position. The pressure uncertainty was about $\pm 0.2\,\mathrm{GPa}$ for the pressures greater than $1.7\,\mathrm{GPa}$, and the corresponding pressure gradient was estimated to be $\sim 0.001\,\mathrm{GPa/\mu m}$.

Theoretical Approach

Group theory was used to determine the number of active vibrational modes and their symmetries. The correlation method [14] was used to associate the site-group species to the factor group species. The space group of α-AlH_3 is $R\,\bar{3}c$ ($\equiv D_{3d}^6$). The aluminum atoms are situated at b sites, where b has three-fold inversion symmetry (S_6), whereas the hydrogen atoms are located at e sites, where e has two-fold symmetry (C_2); b and e are the Wyckoff symbols. The factor group is isomorphic to the point group D_{3d} from which the group representation for the vibrational modes is deduced: $\Gamma = 2A_{1u} + 2A_{2u} + 4E_u + A_{1g} + 2A_{2g} + 3E_g$. There are four Raman active modes ($A_{1g} + 3E_g$) and six IR active modes ($2A_{2u} + 4E_u$); the modes $2A_{1u} + 2A_{2g}$ are inactive or silent.

Results

Raman Spectra Obtained from Sample under Compression

The results of Raman studies of alane under compression are shown in Figure 2. It was observed that there were four Raman lines with various intensities. At ambient temperature and pressure, these were at 512.9, 724.1, 856.8, $1045\,\mathrm{cm^{-1}}$. The lines near 419, 579, and $753\,\mathrm{cm^{-1}}$ belonged to sapphire. The Raman spectrum for the sample totally decompressed to ambient conditions was also included for comparison. As pressure was

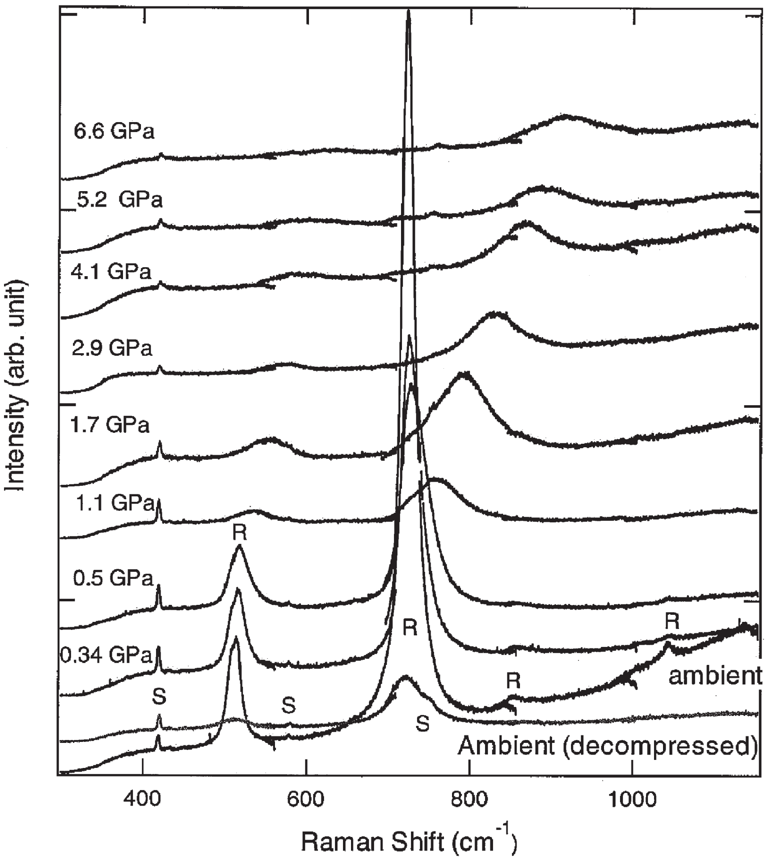

Figure 2. Raman spectra of alane under compression (R = alane Raman, S = sapphire Raman).

increased, Raman shifts increased to higher energies, and lines broadened. Significant broadening began at ~1 GPa. Broadening occurred partly because of the existence of a pressure gradient in the sample and partly because of homogeneous broadening. The sample became translucent as pressure was increased over the range 0.3–6.6 GPa. The translucence greatly facilitated alignment of the sample and improvement of the signal. At about 6.6 GPa the sapphire anvil started showing fine cracks, although the pressure still could be changed and measured. The cell was slowly decompressed to ambient, and the Raman spectra were taken. When totally decompressed, only the two initially intense lines remained observable, but their intensities were much reduced. Their Raman frequencies, however, remained unchanged relative to the ambient spectra obtained before any compression was applied. The alane turned partly dark gray as a result of the interaction with the laser radiation. However, no decomposition was detected, since the two strong Raman lines did not change their frequencies after total decompression. The other two Raman lines were too weak to be observed. It was unlikely that the absence of these was caused by a phase transition, since X-ray structural studies to a pressure of 35 GPa [3], did not observe any phase transition. Throughout the Raman studies, for pressures in the 0.3–6.6 GPa range, the sample remained translucent.

Ambient IR Spectra

The ATR-IR of α-AlH_3 under ambient conditions is shown in Figure 3. It was observed that, unlike the corresponding Raman spectra, the IR spectral lines were broad. The spectra showed

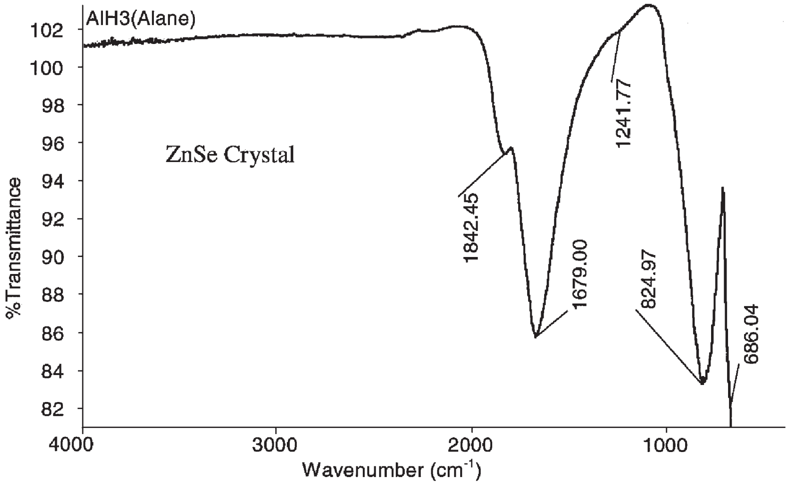

Figure 3. ATR-IR AlH_3 (alane) at ambient.

IR frequencies from about 600 to 1800 cm^{-1}, but the band 600–680 cm^{-1} was too close to the lower limit of the ATR-IR instrument because ZnSe becomes strongly absorbing just below 700 cm^{-1}. Thus only part of this band was observed. The IR frequencies observed in this study were different from those published in 1963 by German researchers [7], which listed frequencies at 1025, 1592, and 1760 cm^{-1} obtained with a Leitz infrared spectrograph. The fact that, in our study, the sample was not mixed with any other material, whereas that of the previous study was placed in Nujol, could not explain these differences. It could not be confirmed that the material reported in [7] was the α polymorph since no X-ray structure determination was provided for the material studied.

Analysis

The Raman frequencies at ambient conditions agreed well with the local maxima (peaks) in the generalized vibrational density of states (GVDS) plot that was deduced from neutron spectroscopy using inelastic neutron scattering (INS) [8]. These peaks were at 63, 88, 105, and 128 meV (i.e., 510.3, 712.8, 850.5, 1037 cm^{-1}; 1 meV = 8.1 cm^{-1}). There was a strong peak in the GVDS at $\sim$76 meV (615.6 cm^{-1}) overlapping the 63 and 88 meV peaks, but this did not correspond to a Raman mode and possibly may be an IR mode since there was significant IR absorption reported at approximately $\sim$640 cm^{-1}, $\sim$680 cm^{-1} [6], and $\sim$614 cm^{-1} [7]. There was less agreement between the observed Raman frequencies and those estimated based on density functional theory (DFT) [9]. According to these calculations, the frequencies and representations of the Raman lines were 490 (E_g), 812 (A_{1g}), 993 (E_g), 1481 (E_g) cm^{-1}. Thus the Raman frequencies agreed only approximately with our experimentally observed values. However, the Raman frequencies observed indeed may be assigned these symmetry representations and thus written in similar manner, as 512.9 (E_g), 724.1 (A_{1g}), 856.8 (E_g), 1045 (E_g) cm^{-1}. The assignment may be made by comparison with α-AlF_3, isomorphous with AlH_3 (i.e., with the same space group $R\bar{3}c$, as well as having Al and F occupy similar sites), which also showed four Raman lines, with similar symmetry labels and similarities in intensities [11]; the aluminum atoms in the trihydride and the trifluoride occupy sites of the same symmetry (b), and the H and the F atoms occupy the same kind of sites (e).

Detailed mode identification has not been pursued in our study. Here we describe some interpretations according to the literature. According to the DFT [9] and INS [8] studies, the vibration modes have been interpreted as the H−Al−H bond-bending deformation of corner-sharing AlH_6 octahedra (DFT) and the hydrogen optic modes (INS); the Raman modes A_{1g} and E_g are contributed by the H atoms only, according to group theoretical analysis: that is, A_{1g} and E_g occur only in $\Gamma(H)$ and not in $\Gamma(Al)$. In the literature on AlF_3 similar Raman modes have been assigned to octahedra rotation, distortion, and stretching [11], but more work needs be done to determine the exact nature of the vibration modes we observed. The experimentally observed Raman frequencies, INS-deduced energies, and DFT-calculated values are summarized in Table 1.

Pressure Coefficients and Mode Grüneisen Parameters

From the Raman spectra of alane under compression, it was observed that the Raman modes hardened as pressure was increased, that is, the Raman shifts increased as pressure was increased. However, the Raman lines at ~419, 579, and

Table 1

Comparison of experimentally observed Raman frequencies at ambient conditions, INS-deduced and DFT-calculated values

Raman mode	Raman frequency (cm^{-1})	INS(cm^{-1})	DFT calculated (cm^{-1})
E_g	512.9	510.3	490
A_{1g}	724.1	712.8	812
E_g	856.8	850.5	993
E_g	1045	1037	1481

753 cm^{-1}, due to sapphire, did not change position with pressure since the bulk of the sapphire anvils were mostly at ambient pressure. From the alane part of the spectra the pressure dependence of the Raman shifts was displayed in Figure 4 and the pressure coefficients (dν/dP) were estimated with a linear fit involving Chi-square minimization using Igor Pro software [13] assuming that the Raman frequencies change linearly with pressure in this pressure range. The fact that there was no abrupt change of slope, in this linear fit, was consistent with the observation that there were no phase transitions [3].

The mode Grüneisen parameter γ_i's were calculated with the expression $\gamma_i = (1/\nu_i)\ (d\nu_i/dP)B$, where ν_i was the Raman mode frequency and B was the isothermal bulk modulus. Using a value of 47.9 ± 1 GPa for B as listed in reference [3], the γ_i values are summarized in Table 2 with the accuracies of the Raman frequencies, pressure coefficients, and mode Grüneisen parameters.

These γ_i values were comparable to the Grüneisen parameter γ_{th}, estimated from thermodynamics with the expression $\gamma_{th} \approx 1/2\ (B')$, where B', was the pressure derivative of the isothermal bulk modulus [15]. B' of alane was $\sim$3.3 [3]. Thus $\gamma_{th} \approx 1.7$ is within the range of our calculated values for the γ_i's. However, rather than comparing an individual γ_i with γ_{th},

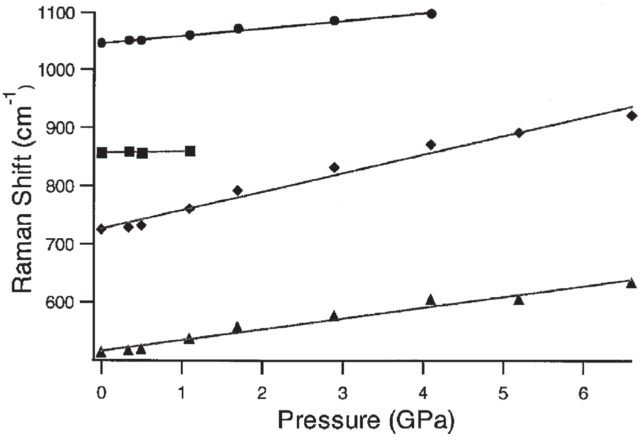

Figure 4. Alane Raman shift pressure dependence.

Table 2
Raman frequencies, pressure coefficients, and mode Grüneisen parameters

Raman frequency (cm^{-1})	$d\nu_i/dP$ (cm^{-1}/GPa)	γ_i
512.9 ± 0.5	18.6 ± 1.2	1.7 ± 0.12
724.1 ± 0.5	31.9 ± 1.7	2.1 ± 0.12
856.8 ± 1	2.6 ± 2.3	0.15 ± 0.13
1045 ± 1	12.9 ± 0.7	0.59 ± 0.03

a more meaningful comparison would have been the weighted average of the γ_i's of the modes with each mode weighted by the contribution of this mode to the total specific heat. This has not been pursued in this study, because the contribution for each mode was not known.

Conclusions

In this study we have observed that under ambient conditions there were four Raman modes with frequencies at 512.9, 724.1, 856.8, 1045 cm^{-1} as predicted by group theory. These Raman frequencies agreed with those vibration energies deduced from inelastic neutron-scattering studies. It was observed that the Raman modes increased in frequency as pressure was increased to a pressure of 6.6 GPa. The mode Grüneisen parameters, deduced from the pressure coefficients, were $\gamma_{512.9} = 1.7$; $\gamma_{724.1} = 2.1$; $\gamma_{856.8} = 0.15$; $\gamma_{1045} = 0.59$. These values were similar to the thermodynamic Grüneisen parameter, approximately 1.7, estimated from the pressure derivative of the isothermal bulk modulus. It was also observed that during the Raman studies α-AlH_3 remained translucent under compression and decompression in the range 0.3–6.6 GPa. The Raman frequencies of the two intense Raman modes were the same at ambient temperature before compression and after total decompression. No phase transitions were indicated in the pressure range studied. This is consistent with results of X-ray structural studies [3]. Modes have not been identified in these Raman studies.

The ATR-IR spectra obtained at ambient above 700 cm^{-1} were different from those published in 1963 for $(\mathrm{AlH}_3)_n$ [7]. However, the material in the published study may be different from that used in our study. Our material was confirmed by X-ray diffraction technique to be the α-AlH_3 polymorph, but the structure of the material in the 1963 study was not verified with *X*-ray diffraction. Modes have also not been identified in the IR studies.

These studies that characterize energetic materials at high pressures are important in field applications and in modeling propellants. The Raman modes at high pressure of alane and the mode Grüneisen parameters are helpful in characterizing the responses and detailed behaviors of this material.

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