NEUTRON SPECTROSCOPY AND THERMODYNAMICAL PROPERTIES OF γ ALANE

Antonov V.E.[*], Graetz J. [(1)], Jensen C.M.[(2)], Kolesnikov A.I.[(3)], Langley W.[(2)]

Insitute of Solid State Physics RAS, 142432 Chernogolovka, Moscow district, Russia

[(1)] Department of Energy Sciences and Technology, Brookhaven National Laboratory, Upton, NY 11973-5000, USA

[(2)] Department of Chemistry, University of Hawaii, Honolulu, HI 96822, USA

[(3)] Spallation Neutron Source, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

FAX: +7 (496) 52 49 701   E-mail: antonov@issp.ac.ru

Introduction

One of the most promising materials for hydrogen storage, aluminium trihydride (alane), has a few different polymorphic modifications. The spectrum of phonon density of states, $g(E)$, was earlier constructed for the α polymorph based on results of inelastic neutron scattering (INS) studies [1]. From the $g(E)$ spectrum, the heat capacity and other thermodynamic properties of α-AlH$_3$ were further calculated at temperatures up to 1000 K [2] much exceeding the temperature 400–450 K of decomposition of the trihydride at ambient pressure.

The present paper reports on an INS investigation of γ-AlH$_3$ prepared using an organometallic synthesis route [3].

Results and discussions

Two samples of γ alane—sample #1 synthesised at BNL and #2 at the University of Hawaii—were studied using the direct-geometry HRMECS spectrometer at the Argonne National Lab, USA. As seen from Fig. 1, the INS spectra, $G(E)$, of the γ-AlH$_3$ samples proved to be very similar in the ranges of both optical (a) and translational (b) modes, so we used the simple average of these spectra as the spectrum of γ alane in further considerations.

As is also seen from Fig. 1, the spectra for the γ samples significantly differ from the spectrum for α-AlH$_3$ measured for comparison. This is because α-AlH$_3$ has a structure built of corner-sharing AlH$_6$ octahedra, while γ-AlH$_3$ is composed of both corner- and edge-sharing octahedra [4]. The first acoustic phonon peak in γ-AlH$_3$ appears at a lower energy and the band of translational modes extends to higher energies (55 *vs*. 42 meV). The bending modes are observed at approximately the same energies 60–140 meV. The Al-H stretching modes in the γ-phase show eight peaks in the range 145 to 265 meV, while in the α-phase, they exhibit only two peaks at 200 and 235 meV.

To get the spectrum $g(E)$ of phonon density of states in γ alane, we (*i*) calculated and subtracted the multi-phonon contribution from the experimental INS spectrum thus producing the one-phonon spectrum of generalized density of states; (*ii*) divided it by the Debye-Waller factor and (*iii*) normalized the translational and optical bands to represent the number of corresponding phonon modes, respectively, 3 and 9.
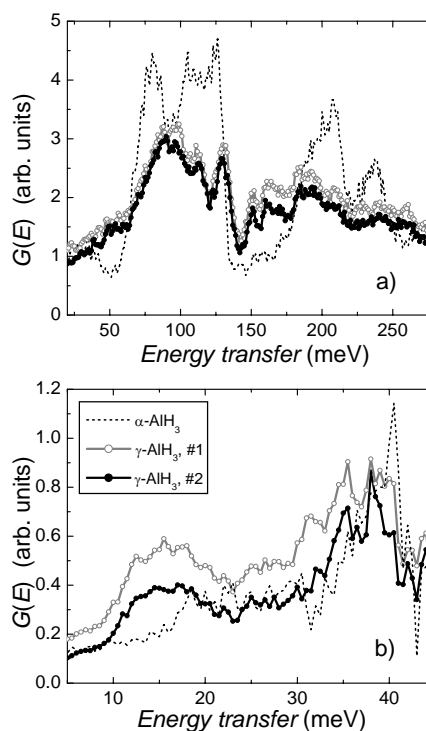

Fig.1. Generalized vibrational density of states $G(E)$ for AlH$_3$ polymorphs measured at 5 K with the HRMECS spectrometer (ANL, USA) using neutrons with the incident energy E_i = 300 meV (a) and 50 meV (b).

In fact, we calculated two differently normalized spectra (Fig. 2), because it was not clear if the peak at 50 meV was due to the translational modes or not. All basic features of the $g(E)$ spectra thus obtained were in good agreement with recent simulations [5].

Figs. 3 and 4 present, respectively, temperature dependences of the heat capacity C_V and Gibbs free energy G^0 of α alane from ref. [2] and those for γ alane calculated using two our $g(E)$ spectra and the spectrum from ref. [5]. Each $G^0(T)$ dependence for γ-AlH$_3$ in Fig. 4 is shifted from that for α-AlH$_3$ by

a constant value of G^{00} calculated from the condition that a $\gamma \rightarrow \alpha$ transition takes place at $T = 373$ K and the enthalpy of this transition is $\Delta H = -2.8$ kJ/mol AlH$_3$ [3]. The negative sign of ΔH indicates that the transition is non-equilibrium and γ-AlH$_3$ should be less stable than α-AlH$_3$ at 373 K.
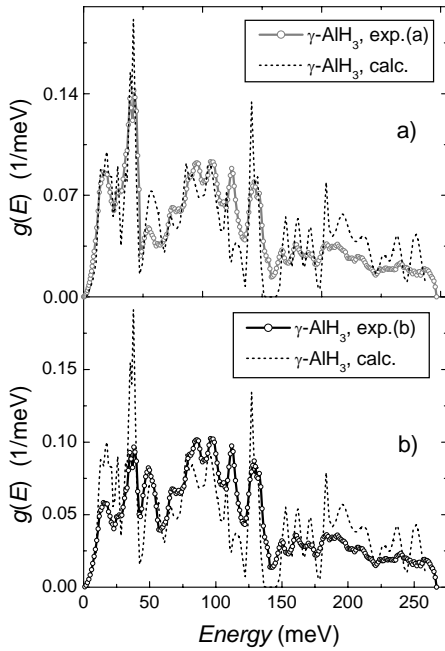

Fig.2. Phonon density of states $g(E)$ for γ-AlH$_3$ obtained from our INS data (solid curves) assuming that the peak at 50 meV originates from bending (a) and translational (b) modes. The dashed curve shows $g(E)$ calculated for γ-AlH$_3$ in [5] and convoluted with the resolution function of HRMECS (dashed curve).
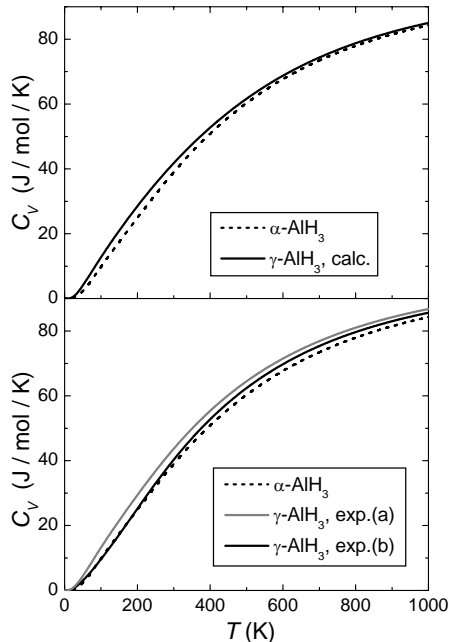

Fig.3. Heat capacity C_V at constant volume calculated from the $g(E)$ spectrum for α-AlH$_3$ [2] (dashed curve) and from the three $g(E)$ spectra for γ-AlH$_3$ shown in Fig. 2 (solid curves).

As one can see from Fig. 4a, the free energy of γ-AlH$_3$ calculated using $g(E)$ from ref. [5] falls below that of α-AlH$_3$ on heating above 430 K. Taking into account the large absolute value of ΔH at 373 K, the reversal of the relative stability of the γ and α phases at a nearby temperature of 430 K is unlikely. The γ phase with the 50 meV peak in the band of bending modes gets more stable than α at 320 K (see the gray curve in Fig. 4b) that contradicts experiment [3]. If the 50 meV peak belongs to the translational band, the γ phase remains less stable than α at temperatures of at least twice as high as that of the experimental $\gamma \rightarrow \alpha$ transition (black curve in Fig. 4b).
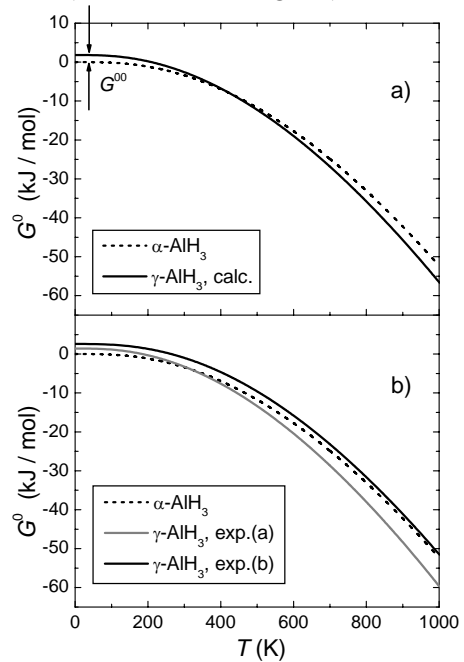

Fig.4. Standard ($P_0 = 1$ bar) free energy $G^0(T)$ for α-AlH$_3$ (dashed curve) and γ-AlH$_3$ (three solid curves) calculated using the corresponding $C_V(T)$ dependences from Fig. 3.

Conclusions

The most likely spectrum of phonon density of states in γ alane is presented by the thick curve in Fig. 2b.

References

1. Kolesnikov AI et al. Phys. Rev. B 2007;76(6): 064302–1-7.
2. Antonov VE et al. J. Phys.: Condens. Matter 2008;20(27):275204–1-10.
3. Graetz J, Reilly JJ. J. Alloys Compds 2006;424: 262-265.
4. Yartys VA et al. Inorg. Chem. 2007;46(4): 1051-1055; Brinks HW et al. J. Alloys Compds 2007;441:364-367.
5. Wang Y et al. Phys. Rev. B 2008;77(1):01410 1–1-8.