

Clarifying bonding nature in aluminum hydride using soft X-ray synchrotron radiation

Hydrogen is an ultimate source of clean energy. The key to utilizing hydrogen as an energy source is to develop materials in which a large amount of hydrogen can be stored and for which the hydrogen storage and release processes can be regulated under pressures and temperatures close to those of atmospheric conditions. Aluminum hydride ($\alpha\text{-AlH}_3$) is a candidate for a hydrogen storage material owing to its large gravimetric and volumetric hydrogen content (10.1 wt% and 149 kgm^{-3} , respectively) [1]. Although $\alpha\text{-AlH}_3$ is lightweight and can store a large amount of hydrogen, high temperature and pressure are required to enable hydrogen storage. To solve this problem, it is essential to understand the bonding nature of aluminum and hydrogen atoms.

Many theoretical studies of the electronic structure of $\alpha\text{-AlH}_3$ have been reported so far. On the other hand, there have been very few experimental studies. Whether the nature of bonding between aluminum and hydrogen atoms is ionic or covalent has not yet been settled in the theoretical research. Therefore experimental studies of the electronic structure are urgently required.

Soft X-ray emission spectroscopy (SXES) and soft X-ray absorption spectroscopy (SXAS) with a total fluorescence yield (TFY) method are feasible

techniques for investigating experimentally bulk electronic structures. These techniques are applicable to the investigation of insulating $\alpha\text{-AlH}_3$. A successful example of their application to an amide hydride, which is a large gap insulator, has been reported recently [2]. Photon-in-photon-out spectroscopy is insensitive to surface conditions and hence has advantages over surface-sensitive spectroscopies, such as photoemission spectroscopy, in measuring bulk electronic structures. SXES and SXAS experiments enable us to measure the occupied and the unoccupied electronic states, respectively, and to obtain the whole feature of the electronic states by combination of their spectra. In addition, one can extract a partial density of states (PDOS) for a specific element by the tuning photon energy to the excitation energy of the target element in the SXES and SXAS experiments.

A polycrystalline sample of $\alpha\text{-AlH}_3$ was synthesized by the hydrogenation of Al metal with hydrogen fluid at 600°C and 8.9 GPa [3]. In order to investigate the change in the electronic structures upon hydrogenation, an Al metal sample with a purity of 6N (Nilaco Corporation, Japan) was also prepared as a reference material. In the present measurements, we focused our interest on the Al $3p$ electronic states

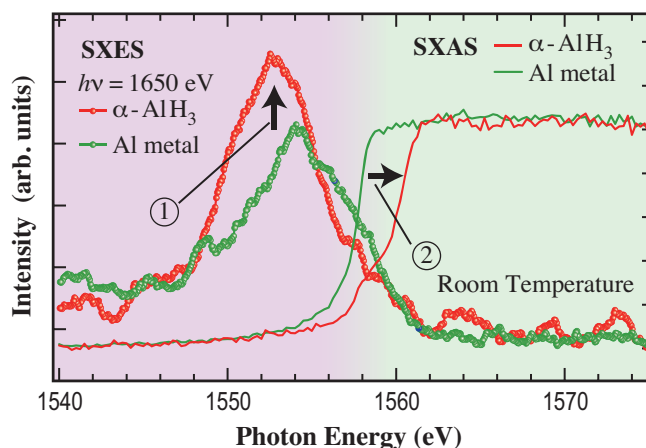


Fig. 1. Electronic states of Al metal (green) and aluminum hydride $\alpha\text{-AlH}_3$ (red) obtained by soft X-ray emission spectroscopy (SXES: closed circles) and soft X-ray absorption spectroscopy (SXAS: solid lines). SXES and SXAS can reveal the occupied and unoccupied electronic states, respectively. The integrated value of the spectral intensity can be considered to be the number of electrons. [6]

of the two samples. The Al 3*p* PDOS in the occupied and unoccupied states were observed by SXES at the Al *K*_β emission (3*p* → 1*s*) and by SXAS at the Al *K* (1*s* → 3*p*) absorption edge, respectively. SXES and SXAS measurements were performed at the experimental station of the soft X-ray beamline **BL27SU** [4]. SXAS spectra were measured by the TFY method. Both the experiments were performed on the same sample at room temperature. Neither cleaning nor treatment of the sample surface was carried out in the vacuum chamber. The energy resolution (ΔE) of the incident photon was set to $E/\Delta E = 3000$. The total ΔE in the SXES experiment was 4 eV from the peak width of the elastic scattering of the incident excitation X-rays.

Figure 1 shows the whole Al 3*p* electronic structures of α -AlH₃ and Al metal obtained by combining the SXES and SXAS spectra. The SXES spectrum of α -AlH₃ is normalized so as to have the same integrated intensity as the SXES spectrum of Al metal at the characteristic *K* α emission at $h\nu = 1486.6$ eV, because one can assume that the *K* α emission has the intensity independent of materials. The SXAS spectrum of α -AlH₃ is normalized so as to be the same spectral height of the SXAS spectrum of Al metal at $h\nu = 1600$ eV. The electronic states of the Al 3*p* PDOS obviously show two significant differences between α -AlH₃ and Al metal. After hydrogenation, the SXES spectral intensity is increased and an energy gap is formed as shown by arrows 1 and 2, respectively. The enhancement of the SXES spectral intensity means that the number of Al 3*p* electrons in the occupied states increases by the hydrogenation. If the Al-H bond is completely ionic, it is expected that the Al 3*p* electrons transfer to the H atom according to the electronegativity [5], namely AlH₃ → Al³⁻ + 3H⁺. However, this assumption is opposite to the observed result that the distribution of the Al 3*p* electrons increases. It is also found

that the band-structure calculation (not shown here) qualitatively reproduces the energy gap and the increase of Al 3*p* electrons upon hydrogenation. The present findings from the experimental and theoretical investigations, namely, that the energy-gap formation and the increase of the Al 3*p* electrons occur simultaneously, suggest that the covalent nature should be significant in the Al-H bond [6]. This clarification will not only contribute to understanding the hydrogen-storage and -release processes of aluminum hydrides but also provide directions for the design of new hydrogen-storage materials based on lightweight and inexpensive aluminum.

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