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Electronic structure of aluminium trihydride studied using soft x-ray emission and absorption spectroscopy

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We have performed soft x-ray emission spectroscopy (SXES) and soft x-ray absorption spectroscopy (SXAS) experiments on aluminum hydride α-AlH_3. The occupied and unoccupied electronic states of the Al $3p$ partial density of states are obtained experimentally. By comparing the data from Al metal and α-AlH_3, a band gap with a few eV is found for α-AlH_3. In addition, the occupied states of α-AlH_3 have a larger spectral intensity than that of Al metal, indicating an increase in the number of electrons with the Al $3p$ character through Al-H bond formations. The results of a band-structure calculation account for the formation of the energy gap and the increase of the Al $3p$ electrons qualitatively. This suggests that a covalent-like nature is important to the Al-H bond in α-AlH_3.

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Aluminum hydride α-AlH_3 is a candidate for a hydrogen storage material due to its large gravimetric and volumetric hydrogen content (10.1 wt% and 149 kgm^{-3}, respectively).[1–4] This hydride possesses a small negative enthalpy of formation (-11.3 kJ/mol H_2)[5] and is metastable at ambient conditions. Dehydrogenation reaction ($AlH_3 \rightarrow Al + 3/2\ H_2$) occurs at moderate temperatures around 600 K.[6,7] The hydrogenation of Al metal drastically changes the fcc metal lattice structure unlike those of transition and rare-earth metals in which absorbed H atoms occupy the interstitial sites of the metal lattices. α-AlH_3 has a hexagonal structure with lattice constants $a = 4.449$ Å and $c = 11.804$ Å (space group $R\bar{3}c$).[8] Each of the Al atoms is surrounded by six H atoms coordinated octahedrally and each of the H atoms is shared with an adjacent AlH_6 octahedron. The electronic structures and the bonding state of α-AlH_3 have been an important subject of experimental and theoretical researches.

Concerning the electronic structure of α-AlH_3, theoretical studies[9–13] have gone ahead of experimental ones. The Al-H bonding properties are investigated by the band overlap population (BOP) analysis using GGA calculations.[12] The BOP value of α-AlH_3 is located at an intermediate value between the ionic Na-H bond in NaH and the covalent Al-H bond in $NaAlH_4$. In the other calculations, however, the occupied states are dominated by the H states while the unoccupied states consist mainly of the Al states. Therefore, it is concluded that the Al-H bond is characterized as an ionic bond.[9,10] The Al-H bond character in α-AlH_3 is still controversial in the theoretical studies.

On the other hand, there have been few experimental studies of the electronic structure of α-AlH_3.[14,15] In photoemission spectroscopy (PES) measurements using a Mg x-ray tube ($h\nu = 1253.6$ eV), the intrinsic occupied electronic states cannot be observed due to an oxide layer with ~5 nm thickness formed on the sample surface, which prevents α-AlH_3 from decomposing even at vacuum conditions.[14] From the Al $L_{2,3}$ electron energy-loss spectrum (EELS) of α-AlH_3, the characteristic features of the unoccupied states are deduced through comparison with those of Al metal and Al_2O_3.[15] However, the whole electronic structures including the occupied states are not obtained by EELS. The obtained experimental information is still insufficient to establish an appropriate understanding of the bonding nature. The observation of bulk electronic structures is highly required.

Soft x-ray emission spectroscopy (SXES) and soft x-ray absorption spectroscopy (SXAS) with a total fluorescence yield (TFY) method are feasible techniques to investigate experimentally the bulk electronic structure. These techniques are applicable to the investigation of insulating α-AlH_3. A successful example of its application to an amide hydride, which is a large gap insulator, has been reported recently.[16] A photon-in-photon-out spectroscopy is insensitive to surface conditions and hence has advantages over a surface-sensitive spectroscopy such as PES 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, we can extract a partial density of states (PDOS) for a specific element by tuning photon energy to the excitation energy of the target element in the SXES and SXAS experiments.

A polycrystalline sample of α-AlH_3 was synthesized by hydrogenation of Al metal with hydrogen fluid at 600 °C and 8.9 GPa.[6] The diameter of the sample was 0.8 mm, sufficiently large for SXES and SXAS measurements. In order to investigate change in the electronic structures by

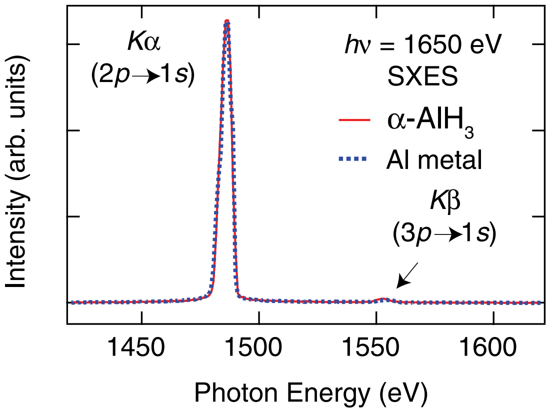

FIG. 1. (Color online) The SXES spectra of α-AlH$_3$ and Al metal excited at $h\nu = 1650$ eV. These spectra are normalized by the intensity of the K_α characteristic x ray ($2p \rightarrow 1s$) at 1486.6 eV. The K_β emission ($3p \rightarrow 1s$), which reflects the Al $3p$ occupied states is observed around 1550 eV.

hydrogenation, an Al metal rod with a purity of 6N (Nilaco Corporation, Japan) was also prepared as a reference material. In the present measurements, we focused our interests on the Al $3p$ electronic states of the two samples. The Al $3p$ PDOS in the occupied and unoccupied states were observed by SXES at the Al K_β emission ($3p \rightarrow 1s$) and by SXAS at the Al K ($1s \rightarrow 3p$) absorption edge, respectively.

SXES and SXAS measurements were performed at the experimental station of soft x-ray beamline BL27SU of SPring-8. SXES spectra were taken with a grazing-incidence flat-field spectrometer.[17,18] SXAS spectra were measured by the TFY method. Both experiments were performed on the same sample at room temperature. Neither cleaning nor treatment of the sample surface was made. 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 SXES spectra of α-AlH$_3$ (solid line) and Al metal (dotted line) obtained at a photon energy of $h\nu = 1650$ eV. These SXES spectra have two structures at 1486.6 and around 1555 eV. The characteristic x-ray emission at 1486.6 eV corresponds to the Al K_α ($2p \rightarrow 1s$). The weak structure around 1555 eV comes from the Al K_β emission ($3p \rightarrow 1s$) and is related to the Al $3p$ occupied PDOS. Although several references can be consulted about the Al L-edge SXES experiment of Al compounds,[19–22] the Al K-edge SXES experiments have been hardly reported.[23,24] In order to compare the occupied Al PDOS between α-AlH$_3$ and Al metal, these SXES spectra are normalized to the peak intensity of the K_α characteristic emission on the assumption that the K_α characteristic x-ray emission has the intensity independent of materials.

Next, the whole electronic spectra are composed by combining the SXES and SXAS spectra. The spectra of α-AlH$_3$ and Al metal are shown in Fig. 2. Here, we explain the normalization procedure for these spectra. First, the SXES spectrum of α-AlH$_3$ is normalized so as to have the same integrated intensity as the SXES spectrum of Al metal at the characteristic K_α emission (see Fig. 1). Secondly, the SXES and the SXAS spectra of Al metal are normalized so that the SXAS spectral height at the edge jump is equal to the SXES spectra height at the maximum, and then the normalized SXAS spectrum of Al metal is drawn together with the SXES spectra on the same scale photon-energy. Finally, the SXAS spectrum of α-AlH$_3$ is normalized so as to be the same spectral height of the SXAS spectrum of Al metal at 1600 eV, and similarly it is added to the graph to complete the whole electronic structures of α-AlH$_3$, which allows direct comparison of the electronic structures between α-AlH$_3$ and Al metal.

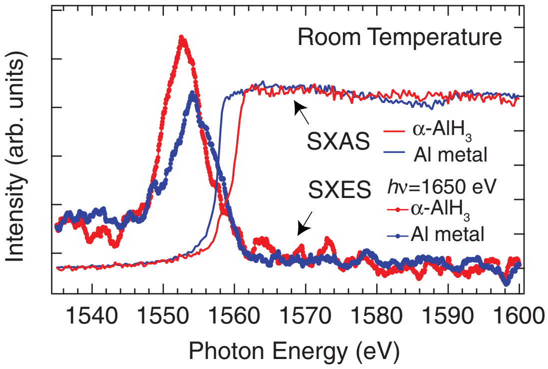

FIG. 2. (Color online) Al $3p$ PDOS of occupied (SXES) and unoccupied (SXAS) states for α-AlH$_3$ (red) and Al metal (blue). The closed circles and solid lines show SXES and SXAS spectra, respectively. The normalization method between these SXES and SXAS spectra is described in the text.

The electronic states of the Al $3p$ PDOS obviously show two significant differences between α-AlH$_3$ and Al metal: the presence of an energy gap and an enhancement of the SXES spectral intensity. From a comparison between SXAS spectra, the energy gap is formed in α-AlH$_3$. The Al $L_{2,3}$ EELS spectrum measured for α-AlH$_3$ shows a shift of the absorption edge toward higher energy in comparison with that of Al metal.[15] This is consistent with the present SXAS results. The magnitude of the energy gap (E_g) can be deduced to be larger than 1.3 eV at least, although we cannot mention having the energy gap or not in the occupied state because of the limitation of the experimental energy resolution. Meanwhile, the bandwidth shows no significant change by the hydrogenation. The Al $3p$ band of α-AlH$_3$ has almost the same width of about 13 eV as that of Al metal within the experimental energy resolution.

Here, let us move onto the enhancement of the SXES spectral intensity by the hydrogenation. The integrated spectral intensity of α-AlH$_3$ is about 1.3 times larger than that of Al metal. It is naturally considered that the number of the Al $3p$ electrons in the occupied states increases by the hydrogenation or the formation of Al-H bonds. If the Al-H bond is completely ionic, it is expected that the Al $3p$ electrons transfer to the H atom according to the electronegativity,[25] namely AlH$_3$ $\rightarrow$ Al^{3-} + 3H^{+}. However, this assumption is opposite to the observed result that the distribution of the Al $3p$ electrons increases.

In order to interpret the enhancement of the spectral intensity of the SXES spectra, we performed a theoretical investigation for the electronic states of α-AlH$_3$ and Al metal using a local density approximation (LDA) band calculation by a linearized-augmented-plane wave method.[26] In the self-consistent calculation for α-AlH$_3$, the muffin-tin (MT)

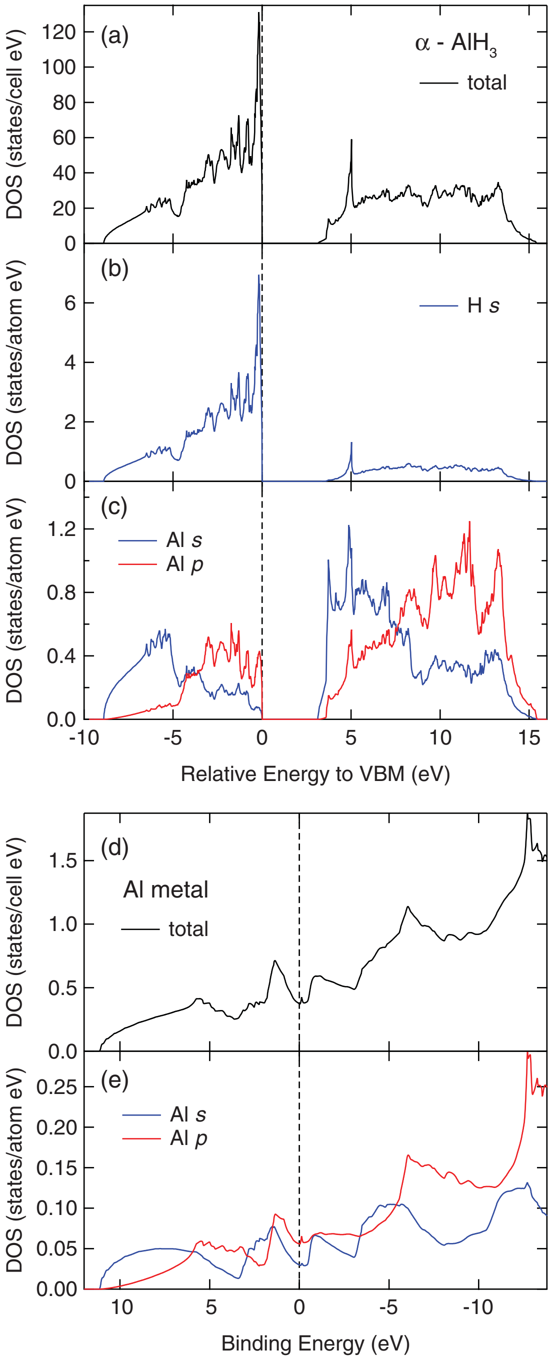

FIG. 3. (Color online) Calculated DOS within LDA. (a) Total DOS, (b) H PDOS, and (c) Al PDOS in α-AlH$_3$ are projected. The energy axis is scaled as the relative energy to valence-band maximum (VBM). (d) Total DOS and (e) Al PDOS in Al metal are also projected.

radii at both the Al and the H sites were fixed at $R_{\mathrm{MT}} = 0.858$ Å. This corresponds to half of the Al-H bond-length of 1.715 Å.[8] The calculated electronic structure of α-AlH$_3$ is shown in Figs. 3(a)–3(c), giving an energy gap of $E_g = 3.1$ eV. The magnitude of the E_g is close to 3.5 eV from the GW calculation[9] and larger than 2 eV from the pseudopotential density-functional calculation.[11] Although the E_g dependents on approximation or models, electronic structures with similar features in shape are obtained from these calculations. We calculated the number of the electrons, which are characterized as the Al 3p occupied PDOS within the MT sphere centered at Al nucleus, to be 0.14.

Next the occupied number of the Al 3p electrons was calculated for Al metal with the same MT radius ($R_{\mathrm{MT}} = 0.858$ Å) at Al site as in α-AlH$_3$. Figures 3(d) and 3(e) show the electronic structure of Al metal. A number of 0.03 was obtained for the Al 3p electrons of Al metal. This small number implies that the electrons are well delocalized in the Al metal lattice. The large number of the Al 3p electrons in α-AlH$_3$ indicates a localization of the electrons in the AlH$_6$ octahedron units.

In the present experiment, the integrated spectral intensity of α-AlH$_3$ is about 1.3 times larger than that of Al metal. We obtain a value of 4.6 as an enhancement factor from the calculated results, if we assumed simply the ratio of the numbers of electrons 0.14 (α-AlH$_3$)/0.03 (Al metal) to be proportional the enhanced magnitude. This value is very much larger than the experimentally obtained value, but qualitatively explains the change in the bonding nature of Al 3p electrons by hydrogenation. The itinerant electrons in the metal become localized as a result of formation of the hybridized states between Al 3p and H 1s orbitals.

The theoretical interpretation on the Al-H ionic bond in α-AlH$_3$ is based on an idea that the population of the H 1s PDOS of the occupied states is much larger than that of the unoccupied states.[9,10] The changes of the electronic states through the formation of the Al-H bond by the hydrogenation are crucial to understand the nature of the Al-H bond. The present findings from the experimental and theoretical investigations, namely that the energy-gap formation and the increase of the Al 3p electrons occur simultaneously, suggest that the covalent nature should be significant in the Al-H bond.

In summary, SXES and the SXAS experiments have been performed in order to grasp the electronic structure of α-AlH$_3$ and the change of the electronic structures associated with the hydrogenation. By comparing Al metal with α-AlH$_3$ in the electronic structures, two significant differences between Al metal and α-AlH$_3$ were observed. First, α-AlH$_3$ has an energy gap of a few eV. Second, the spectral intensity of the Al 3p PDOS in the occupied states of α-AlH$_3$ becomes larger than that of Al metal. It is considered that the number of the Al 3p electrons in the occupied states increases. The band-structure calculation reproduces qualitatively the energy gap and the increase of Al 3p electrons. This suggests a covalent-like nature of the Al-H bond in α-AlH$_3$.

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