Development of in-situ resonant soft X-ray Raman scattering on Mg-based hydrogen storage alloys

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Introduction

Mg_2Ni, one of typical Mg-based hydrogen storage alloys, show excellent hydrogen storage properties; 3.6 wt. % hydrogen absorption and the low desorption temperature ~ 180 C. However it is still necessary to improve the both hydrogen storage capacity and desorption temperature. For the design of better materials, the elucidation of the hydrogen absorption and desorption mechanisms from the viewpoint of the electronic structure is important. The experimental investigation on the electronic structure of Mg_2Ni has a difficulty, that is, in-situ measurement in an ambient condition is required. The reason is that Mg_2Ni desorbs hydrogen quickly when it is put in a vacuum, in which ordinary photoemission spectroscopy is performed. Therefore the ambient condition means hydrogen atmosphere with the pressure near ~ 0.1 MPa. To solve this problem, the use of X-ray, which has a high penetrativity for the gas atmosphere, has been tried previously. Some results of in-situ X-ray absorption spectroscopy (XAS) have been reported on Mg_2Ni and its hydride [1,2], and the structure of the unoccupied states were revealed. On the other hand, we adopted high resolution soft X-ray Raman scattering to investigate the electronic structure below Fermi level and furthermore details of excited states. In the last beam-time the components for the in-situ measurement in the gas atmosphere was still under construction, so that we checked the feasibility the measurements from the viewpoint of signal-noise ratio in the case of the Ni *L*-edge excitation.

Experimentals

The Mg_2Ni sample is a thin film (t = 40 nm and covered by 5 nm Pd cap layer) deposited on the Si substrate by DC magnetron sputtering. The soft X-ray Raman scattering measurements were done in BL-07LSU beam-line in SPring-8. Ni *L*-edge is resonantly excited by using the photon energy from 830 up to 890 eV. The sample is put in a vacuum. The scattered X-ray was detected by CCD via a diffraction grating. XAS was taken by means of both electron yield (EY) and fluorescence yield (FY) detected by a photodiode.

Results and Discussion

Fig. 1 (left) shows the XAS profiles taken by the fluorescence yield (FY) and electron yield (EY). The main peaks of L_3 and L_2 are seen at ~ 850 and ~ 867 eV, respectively. The broad satellite peaks are also visible at ~ 857 and 874 eV. We can see that the intensities of the satellite peaks are relatively large in EY profile compared to those in FY profile. The difference between the FY and EY reflects the difference of electronic structure between the near surface region and bulk. Our interest is focused on the bulk electronic structure of the Mg_2Ni thin film, so that, the FY profile gives us the desirable information. The inhibition of the satellite peak intensity means the suppression of the many-body effect in the electron excitation typically seen in Ni. These XAS results show that the advantage of X-ray emission spectroscopy (XES) for the bulk-sensitive measurement is useful for our purpose.

Fig.1 (right) shows the XES profiles taken with four different photon energies: 850.2, 856.8, 867.5 and 874.1 eV. In the profile with 850.2 eV we can see only single peak with symmetrical line shape. The profile with 856.8 eV, which corresponds to the satellite of L_3, shows negligibly small satellite. This result is consistent with the XAS results with FY. In the profile with 867.5 eV photon shows the second peak of $L\beta_I$. The last profile with 874.1 eV photon shows no satellite as well as that with 856.8 eV photon. These results also indicate that the many-body effect of Ni photoexcitation is well suppressed in Mg_2Ni bulk region. We notice that in the two profiles with 867.5 and 874.1 eV there are shoulder like features beside the both $L\alpha_I$ and $L\beta_I$. The energy level these shoulders are significantly different from those of satellite seen in XAS profiles. As a future work we will assign these fine structures observed in XES profiles.

Conclusion

XAS and resonant soft X-ray scattering spectroscopy were done on the thin Mg_2Ni film in BL-07LSU in Spring-8. With the vacuum condition the signal of emitted X-ray is clearly detected, so the sensitivity is good enough for our experimental purpose. As a next step, we will try the same measurement with SiN partition membrane for the measurement with ambient condition.

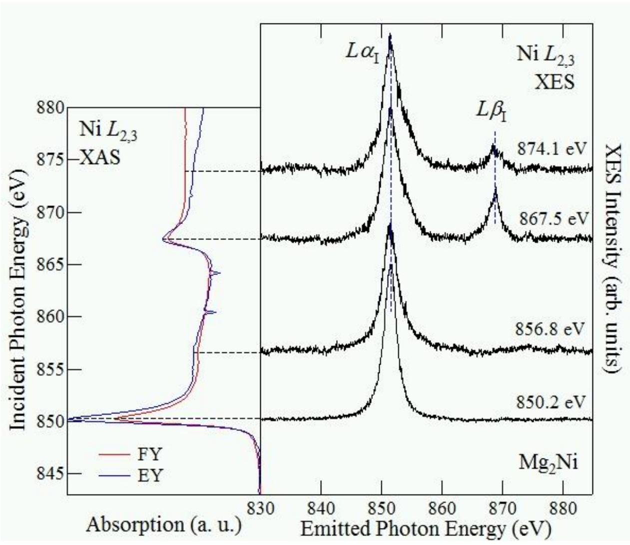

Fig. 1. (left) L-edge XAS profiles of the Mg_2Ni thin film taken by fluorescence yield (red) and electron yield (blue). (right) XES profiles of the Mg_2Ni thin film taken with the four different excitation photon energies.

References

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