BL-7C / 2025G607

Electronic Structure Study of $Dy_{65}Ni_{35}$ metallic glass by means of X-ray Raman Scattering.

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The rejuvenation effect induced by temperature cycling in metallic glasses was reported by Ketov *et al.* [1]. In the present study, changes in electronic structure associated with this rejuvenation effect were investigated for $Dy_{65}Ni_{35}$ metallic glass using X-ray Raman scattering (XRS) [2].

$Dy_{65}Ni_{35}$ metallic glass samples was prepared in two different states: an as-quenched sample (AQ), which had been kept for a long period after vitrification, and a rejuvenated sample (RJ), which had undergone a rejuvenation treatment prior to the measurements. The XRS measurements were carried out at BL-7C of the Photon Factory using the X-ray emission spectrometer "Escargot". The scattered photons were analyzed with an InSb(444) crystal analyzer and detected using a position-sensitive proportional counter (PSPC). Measurements were performed near the Ni $K\alpha$ fluorescence line at the Ni K absorption edge and near the Dy $L\alpha$ fluorescence line at the Dy L_3 absorption edge. XRS spectra were obtained from the measured X-ray emission spectra (XES) as energy-loss spectra.

Figure 1 shows the Ni K-edge high-energy-resolution fluorescence-detected (HERFD) XAFS spectra, obtained by plotting XES intensity as a function of incident photon energy. The spectra for the AQ (black) and RJ (red) samples are superimposed. The main absorption structure is attributed to transition into Ni 4p states, whereas the pre-edge feature is assigned to transitions involving Ni 3d states, which become partially allowed through hybridization effects. The XES measurements were mainly performed in the vicinity of this absorption edge region.

Figure 2 shows the XRS spectra measured at the Ni K edge for $Dy_{65}Ni_{35}$ metallic glass. The spectra of the AQ (dashed line) and RJ (solid line) samples are overlaid. The XRS spectra originated from inelastic scattering process associated with Ni $2p^5 3d^{n+1}$ excitations. Consequently, spectral features corresponding to the $2p_{3/2}$ and $2p_{1/2}$ core-hole states are observed.

A comparison of the two spectra reveals a clear difference in peak position. The XRS peaks of AQ sample are shifted toward higher energy loss compared with those of RJ sample. Interestingly, this shift is opposite to the trend observed for the pre-edge feature in the HERFD-XAFS spectra shown in Fig. 1. This result suggests that the rejuvenation process modifies the local electronic structure around Ni atoms in $Dy_{65}Ni_{35}$ metallic glass.

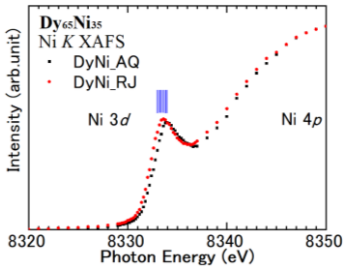

Fig. 1: Ni K-edge HERFD-XAFS spectra of $Dy_{65}Ni_{35}$ metallic glass. A shift of the pre-edge peak associated with the Ni 3d states is observed between the AQ and RJ samples. The vertical bars denote excitation energies of XRS measurements.

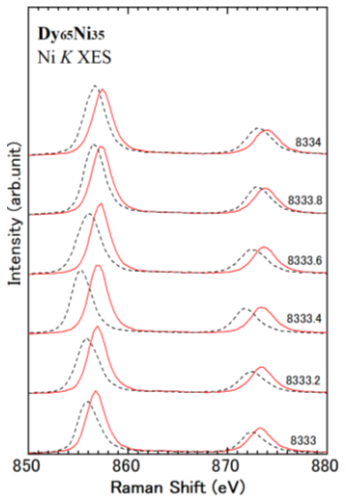

Fig. 2: Comparison of the Ni K-edge resonant XRS spectra of $Dy_{65}Ni_{35}$ metallic glass before and after rejuvenation. Solid and dashed lines correspond to the RJ and AQ samples, respectively. The maximum peak shift is observed at an excitation energy of 8333.4 eV.

Further analysis, including theoretical calculations, will be required to clarify the relationship between the observed spectral changes and the rejuvenation-induced structural modifications.

[1] S.V. Ketov, *et al.*, Nature 524, 200 (2015).
[2] Y. Tezuka, *et al.*, J. Phys. Soc. Jpn. **83**, 014707 (2014).

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