

Changes in Electronic States in Gd-TM metallic glasses Rejuvenated by Temperature Cycling

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Rejuvenation in glasses is defined as an excitation to a higher energy state by an external stress, the opposite of the usual relaxation by thermal annealing. A rejuvenation effect by a temperature cycling in metallic glasses (MG) was recently reported by Ketov *et al.* on a $\text{La}_{55}\text{Ni}_{10}\text{Al}_{35}$ bulk MG [1]. They found such a rejuvenation effect by cycling between liquid N_2 and room temperatures in several macroscopic properties. According to their interpretation, the thermal expansion coefficient has a distribution over a glass sample if it is not elastically homogeneous. By repeated temperature changes, the different magnitudes of thermal expansion at different positions in a glass induces shearing forces, and as a result, a rejuvenation effect occurs in the glass. They called this ‘Rejuvenation of metallic glasses by non-affine thermal strain’ [1]. The validity of this picture is the subject of intensive debate.

Hufnagel reviewed thermal cycling rejuvenation effect, named as ‘cryogenic rejuvenation’, and suggested that non-affine deformation must be caused on an atomistic length scale [2]. The extent of the heterogeneity of glasses can be judged by the magnitude of so-called β -relaxation peak in dynamical mechanical analysis (DMA) spectra, and large peaks were detected in Gd-transition metal (TM) glasses by Yamasaki [3]. By referencing these ideas and results, we recently measured high energy x-ray diffraction (HEXRD) and anomalous x-ray scattering (AXS) on a $\text{Gd}_{65}\text{Co}_{35}$ metallic glass by comparing before and after the temperature cycling, and the structural data were analyzed by reverse Monte Carlo modeling [4]. Tiny but clear structural changes are observed by HEXRD in the nearest neighboring region of the real space pair distribution function. Partial structural information obtained by AXS reveals that slight movements of the Gd and Co atoms occur in the first- and second peaks in the nearest neighboring shells around the central Gd atom. We expect that electronic structures may be largely affected by these structural changes by the cryogenic rejuvenation.

In this series of experiments, we carried out photoemission and inverse-photoemission spectroscopies (PES and IPES) on $\text{Gd}_{65}\text{TM}_{35}$ (TM = Co and Ni) metallic glasses to clarify the rejuvenation effects in the valence- and conduction band densities of states (DOSs) in these glasses, respectively. Master $\text{Gd}_{65}\text{TM}_{35}$ ingots were manufactured by arc-melting a mixture of pure Gd and TM metals in an Ar atmosphere. The purities of Gd, Co, and Ni were 99.95, 99.999, and 99.999 at.%, respectively. Glassy foils with a thickness of about 20 μm and width of about 2 mm were prepared by melt spinning with a single Cu roll in a pure Ar atmosphere. The concentration was confirmed to be within 0.5 wt.% of the nominal values by electron-probe micro-analysis. A thermal cycling treatment was made between liquid N_2 and room temperatures 40 times, and all the experiments were performed for the same sample foils before and after the above temperature cycling.

The PES spectra were measured using a spectrometer installed at BL-7 of Hiroshima Synchrotron Radiation Center (HSRC). Ultraviolet photons generated from a compact electron-storage ring (HiSOR) were monochromatized with a Dragon-type monochromator, covering the incident photon energy, $h\nu$, values from 20 to 450 eV. A PES spectrometer with a hemispherical photoelectron energy-analyzer (GAMMA-DATA, SCI- ENTA SES2002) attached to the analyzer chamber under the ultrahigh vacuum below 1×10^{-8} Pa at the end-station of BL-7, was used for the PES experiments. The overall energy resolution, ΔE , of the spectrometer was about 0.1-0.5 eV depending on the $h\nu$ values of 20-450 eV. All the PES spectra were collected at room temperature. Clean surfaces were in situ obtained by sputtering the samples with Ar^+ ions in a sample preparation chamber with the base pressure below 1×10^{-8} Pa. The energies of all spectra were defined with respect to the Fermi energy, E_F , of the sample or a freshly evaporated Au film.

The IPES experiments were carried out at the resonant IPES spectroscopy (RIPES) station in the HSRC. The self-developed IPES spectrometer is equipped with a low-energy electron gun, a non-periodic spherical grating, and a one-dimensional photon detector. The total energy resolution was ~ 0.5 eV at the electron gun energy E_k of 50 eV. The energy of the IPES spectra is referred to E_F , determined from the Fermi edge of the IPES spectra of a Au film. All the IPES experiments were also carried out at room temperature. Clean surfaces were in situ obtained by scraping the samples with a diamond file in a sample preparation chamber attached with the analyzer one, both of which were kept under ultrahigh vacuum below 1×10^{-8} Pa.

Left panel of Fig. 1 shows the valence-band PES spectra on the $\text{Gd}_{65}\text{Co}_{35}$ glass at $h\nu$ of 40-230 eV before (blue curves) and after (red curves) the cryogenic rejuvenation. The spectral features drastically change with varying $h\nu$. Right panel of Fig. 1 shows the $h\nu$ dependence of photoionization cross-sections of Gd 4f, 5d, and 6s, and Co 3d and 4s electrons. By taking this figure into account, the peaks in the ranges around -5 and -8 eV are mainly composed of the Co 3d and Gd 4f electrons, respectively. By the cryogenic rejuvenation, only the Co 3d peak largely decreases.

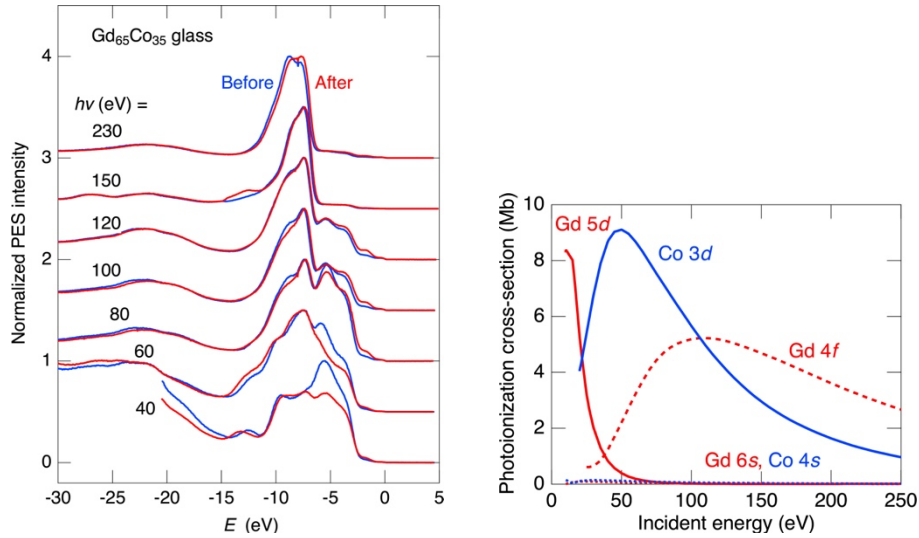


FIGURE 1. (Left) Valence-band PES spectra on $\text{Gd}_{65}\text{Co}_{35}$ glass before (blue curves) and after (red curves) the cryogenic rejuvenation. (Right) Incident photon energy dependence of the photoionization cross-sections of Gd 4f, 5d, and 6s, and Co 3d and 4s electrons.

Left and right panels of Fig. 2 show the Gd 4d and Co 3p core-level PES spectra on the $\text{Gd}_{65}\text{Co}_{35}$ glass measured at $h\nu = 230$ eV. By the temperature cycling, the peak in the Gd 4d spectrum at about -142 eV slightly shifts towards the shallower energy direction, while the peak in the Co 3p spectrum at about -60 eV looks mostly unchanged, suggesting the chemical mature of the Gd atoms may be slightly changed reflecting the structure changes by the rejuvenation.

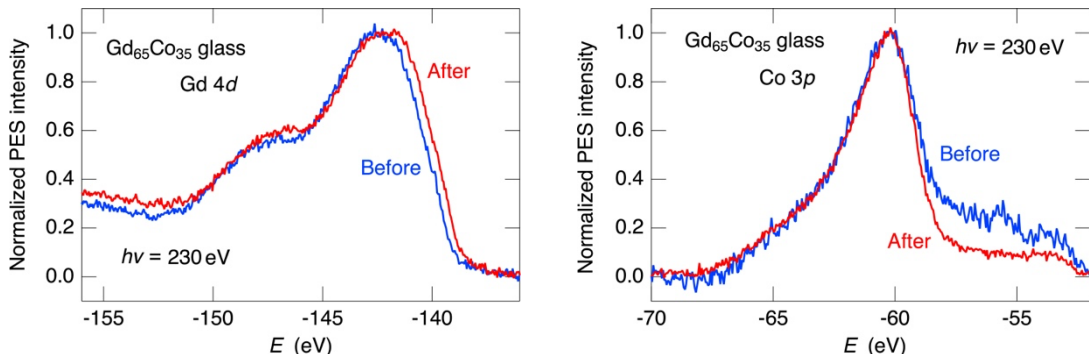


FIGURE 2. Gd 4d (left) and Co 3p (right) core-level PES spectra on $\text{Gd}_{65}\text{Co}_{35}$ glass before (blue curves) and after (red curves) the cryogenic rejuvenation.

Left and right panels of Fig. 3 show the conduction-band IPES spectra on the $\text{Gd}_{65}\text{Co}_{35}$ and $\text{Gd}_{65}\text{Ni}_{35}$ glasses before (blue curves) and after (red curves) the cryogenic rejuvenation, respectively. As clearly seen in the figures, the empty-state spectra of $\text{Gd}_{65}\text{Co}_{35}$ and $\text{Gd}_{65}\text{Ni}_{35}$ glasses resemble each other. The prominent peak at about 7 eV shifts to about 5.5 eV and becomes sharper and higher in the height. Since the spectra of these glasses are very similar, the origin of this peak may be the Gd atoms.

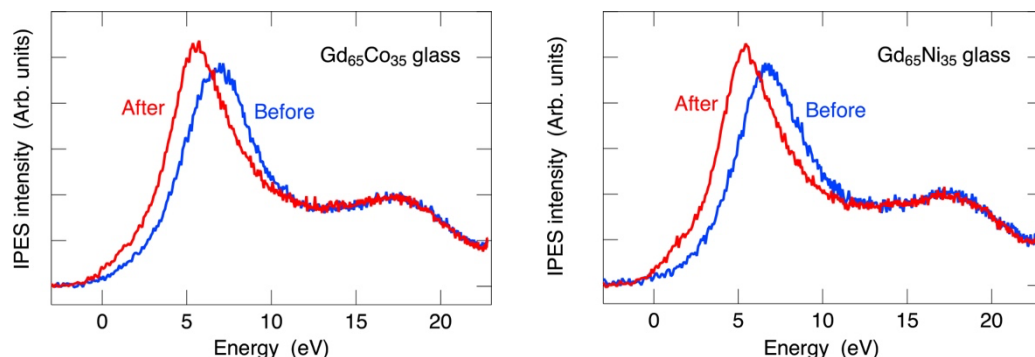


FIGURE 3. Conduction-band IPES spectra on $\text{Gd}_{65}\text{Co}_{35}$ (left) and $\text{Gd}_{65}\text{Ni}_{35}$ (right) glasses before (blue curves) and after (red curves) the cryogenic rejuvenation.

In addition to these works, we measured soft x-ray absorption and emission spectroscopies near the Co and Ni $2p$ - $3d$ resonances, and the $3d$ partial DOS are obtained. The results are under analyzing. Moreover, an *ab-initio* molecular dynamics simulation is planned to obtain further on the atomic and electronic changes by the cryogenic rejuvenation on the Gd-TM glasses.

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