Study of photoinduced valence dynamics in \( \text{EuNi}_2(\text{Si}_{0.21}\text{Ge}_{0.79})_2 \) through time-resolved X-ray absorption spectroscopy

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The photoinduced valence dynamics of \( \text{EuNi}_2(\text{Si}_{0.21}\text{Ge}_{0.79})_2 \) are investigated using time-resolved X-ray absorption spectroscopy for \( \text{Eu} M_5 \)-edge. Through the pump-probe technique with synchrotron X-ray and Ti:sapphire laser pulse, a photoinduced valence transition is observed from Eu\(^{3+}\) to Eu\(^{2+}\). Because the lifetime of a photoinduced state can be up to 3 ns, a metastable state is considered to be realized. By comparing the experimental results with the theoretical calculations, the photoinduced valence transition between Eu \( 4f \) and conduction electrons is quantitatively evaluated.

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The unique phenomena exhibited by \( 4f \) electron systems, such as valence fluctuation, valence transition, and the Kondo effect, have drawn the attention of the scientific community. These phenomena originate from the hybridization between \( 4f \) electrons and conduction electrons [1]. Recently, valence fluctuation and transition in Ce- and Yb-based compounds have reportedly exhibited unconventional superconductivity and non-Fermi-liquid behavior [2, 7]. In addition, the valence fluctuation has been related to quantum critical phenomena [8]. Therefore, the mechanisms of valence fluctuation and transition are germane to the understanding of \( 4f \) electron systems.

For the study of valence fluctuation and the valence transition, Eu compounds are one of the most suitable specimens due to their significantly large valence change. Valence fluctuation and valence transition have been observed between Eu\(^{2+}\) (\( 4f^7 \), \( J = 7/2 \)) and Eu\(^{3+}\) (\( 4f^6 \), \( J = 0 \)) ions [9–21]. The transition of Eu mean valence occurs by external stimuli such as temperature [1, 11, 12, 14–21], magnetic field [13, 15, 20], and/or pressure [14, 16]. The detection of valence transitions was achieved using the Eu \( M_5 \)-edge X-ray absorption spectroscopy (XAS) [15, 19]. However, the interaction of the compounds with photon irradiation is not fully understood. Photon-controlled hybridization between the \( 4f \) and conduction electrons may help realize a novel state and unravel more information on electron–photon interaction. Therefore, in this study, the photoinduced dynamics of electronic structures were investigated.

Extensive studies on photoinduced transition in strongly correlated \( 3d \) transition metal compounds were performed using pump-probe X-ray spectroscopies, revealing dynamics such as insulator-to-metal transition [22, 26]. These techniques involve controlling the time difference between a pump light, such as an visible laser pulse, and a probe light, such as a synchrotron radiation X-ray pulse, to detect the time-dependent variation of photon-induced electronic structures. In the soft X-ray region, the \( 3d \) states were directly observed through the \( 2p \rightarrow 3d \) resonance [25]. As for the \( 4f \) rare-earth compounds, the spin states and the hybridization between \( 4f \) electrons and conduction electrons were studied via resonant X-ray diffraction with \( 3d \rightarrow 4f \) resonance [27] and reflectivity measurements [28]. Although the valence of \( 4f \) electron systems were clearly distinguished in X-ray absorption spectroscopy (XAS) spectra, the valence dynamics were not observed via XAS measurements. Therefore, the photoinduced valence dynamics were investigated using time-resolved soft X-ray absorption spectroscopy (Tr-XAS).

For the study of photoinduced valence dynamics, \( \text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2 \) with \( x = 0.79 \) was selected as it exhibits a large valence change (\( \sim 0.6 \)), and the valence transition occurs at a relatively high temperature (\( \sim 84 \) K) [21]. As the surface of \( \text{EuNi}_2(\text{Si}_{0.21}\text{Ge}_{0.79})_2 \) is sensitive to oxygen, i.e., it tends to get oxidized, the polycrystalline samples were fractured prior to the measurements in an ultra-high vacuum chamber at the possible lowest temperature (\( \sim 40 \) K). The static XAS and Tr-XAS measurements were performed at BL07LSU of SPring-8 [26, 29]. For the static XAS of Eu \( M_5 \)-edge, the measurements were performed at 40 K by the total electron yield (TEY) mode with an ammeter. Because the response time of an ammeter is larger than the order of ps, the partial electron yield (PEY) mode was instead used with a microchannel plate (MCP) detector for Tr-XAS [26].

In the first step, the static XAS measurement of \( \text{EuNi}_2(\text{Si}_{0.21}\text{Ge}_{0.79})_2 \) was performed using the TEY mode. Figure 1 shows the Eu \( M_5 \)-edge TEY XAS spectrum at 40 K. It can be observed that the arrowed peaks are at 1129.6 eV and 1131.5 eV, which correspond to the main peaks of Eu\(^{2+}\) and Eu\(^{3+}\), respectively. The shape of the spectrum is in good agreement with that in Ref. [19], indicating the fine quality of the fractured sample surface.
Based on the result of static XAS, Tr-XAS measurements were performed using the pump-probe technique. The schematic diagram of the experimental setup is shown in Fig. 2(a). A Ti:sapphire laser pulse (hν = 1.5 eV, repetition rate = 1 kHz, width = 50 fs) was adopted as the pump light for this study. As a probe light, a synchrotron soft X-ray pulse (an isolated bunch in the H-mode of SPring-8: a single bunch + a bunch train) with energy near Eu M₂-edge was used. The spot size of the X-rays and Ti:sapphire laser is ∼100 μm × 5 μm and ∼600 μm × 600 μm, respectively. As the area irradiated by synchrotron X-ray is fully exposed by the laser irradiation, the dynamics induced by the pure laser incidence were probed. By varying the delay time between the X-rays and Ti:sapphire laser, the pump-probe technique was performed using the pump-probe technique. The incident visible laser and X-ray were considered to be noises associated with the laser irradiation, indicating a photoinduced valence transition between Eu 4f and its conduction electrons. The timescale of photoinduced valence dynamics was also evaluated using the following function

\[ I(t) = I_1 \exp(-t/\tau_{\text{change}}) + I_2[1 - \exp(-t/\tau_{\text{recovery}})] + 1 - I_1. \]

(1)

Because the time resolution of Tr-XAS is ∼50 ps, the
function was convoluted with the Gaussian response function ($\tau_{\text{Gauss}} = 50$ ps). From the fitting results represented by solid lines in Fig. 3(a), $\tau_{\text{change}}$ was found to be faster than 50 ps and $\tau_{\text{recovery}}$ was $\sim$3 ns. As the timescale of valence transition was much longer than a few ps, reported for YbAgCu$_4$ and YbInCu$_4$ via photoinduced reflectivity measurements [28], a photo-induced metastable state may be realized in EuNi$_2$(Si$_{0.21}$Ge$_{0.79}$)$_2$.

The laser fluence dependence was also investigated. For those measurements, the delay time was fixed at 0.07 ns because the biggest changes were observed at that delay time. Figure 3(b) shows the laser fluence dependence of XAS intensity probed at the peak energies of Eu$^{2+}$ (1129.6 eV) and Eu$^{3+}$ (1131.5 eV). The fluence dependence can be fitted by a straight line, and there is no threshold, such as the photoinduced insulator-to-metal transition [23], which indicates that the valence of Eu can change by weaker laser fluence. However, the valence change by temperature should have a threshold because the valence of Eu changes drastically near the transition temperature, as shown in Ref. [21]. Therefore, a unique photoinduced valence transition was considered.

To investigate the photoinduced valence dynamics in further detail, the PEY XAS spectra were measured at different delay times. Figure 4 illustrates the Eu $M_5$-edge PEY XAS spectra at delay times $=-0.23$ ns, 0.07 ns, 0.87 ns, 4.87 ns, and 9.87 ns. The peaks at 1129.6 eV and 1131.5 eV correspond to the main peaks of Eu$^{2+}$ and Eu$^{3+}$, respectively. The theoretical spectra were obtained by intra-atomic multiplet calculations of Eu$^{2+}$ and Eu$^{3+}$ from Ref. [18].

Figure 5 (a) shows the comparison of experimental Eu $M_5$-edge PEY XAS spectra at various delay times with the theoretical spectra. The valence of Eu was evalu-
The mean valence of Eu evaluated by the calculation. The error bars are (solid lines). (b) The time-dependent variation of mean valence for Eu evaluated by comparing it with the linear combinations of the theoretical valences for Eu at various delay times are shown in Fig. 4.

FIG. 5: (Color online) (a) Comparison between the experimental Eu $M_2$-edge PEY XAS spectra of EuNi$_2$(Si$_{0.21}$Ge$_{0.79}$)$_2$ at various delay times (dotted lines), and the theoretical spectra reproduced by the linear combinations of Eu$^{2+}$ and Eu$^{3+}$ (solid lines). (b) The time-dependent variation of mean valence of Eu evaluated by the calculations. The error bars are obtained from the variation of the reference bunch spectra in Fig. 4.

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