












4*f* electron temperature driven ultrafast electron localizationKohei Yamagami ^{1,*}, Hiroki Ueda ², Urs Staub ³, Yujun Zhang ^{4,†}, Kohei Yamamoto^{5,‡}, Sang Han Park ⁶, Soonnam Kwon ⁶, Akihiro Mitsuda ⁷, Hirofumi Wada ⁷, Takayuki Uozumi⁸, Kojiro Mimura ⁸, and Hiroki Wadati ^{4,9}¹*Institute for Solid State Physics, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581, Japan*²*SwissFEL, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland,*³*Swiss Light Source, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland*⁴*Department of Material Science, Graduate School of Science, University of Hyogo, 3-2-1 Kouto, Kamigori-cho, Ako-gun, Hyogo 678-1297, Japan*⁵*Institute for Molecular Science, Myodaiji, Okazaki, Aichi 444-8585, Japan*⁶*PAL-XFEL, Pohang Accelerator Laboratory, 77 Cheongam-Ro, Nam-Gu, Pohang, Gyeongbuk 37673, Republic of Korea*⁷*Department of Physics, Kyushu University, Motoooka 744, Nishi-ku Fukuoka 819-0395, Japan*⁸*Department of Physics and Electronics, Osaka Metropolitan University, 1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan*⁹*Institute of Laser Engineering, Osaka University, 2-6 Yamadaoka, Suita, Osaka 565-0871, Japan* (Received 27 October 2023; revised 9 February 2024; accepted 4 March 2024; published 29 April 2024)

Valence transitions in strongly correlated electron systems are caused by orbital hybridization and Coulomb interactions between localized and delocalized electrons. The transition can be triggered by changes in the electronic structure and is sensitive to temperature variations, applications of magnetic fields, and physical or chemical pressure. Launching the transition by photoelectric fields can directly excite the electronic states and thus provides an ideal platform to study the correlation among electrons on ultrafast timescales. The $\text{EuNi}_2(\text{Si}_{0.21}\text{Ge}_{0.79})_2$ mixed-valence metal is an ideal material to investigate the valence transition of the Eu ions via the amplified orbital hybridization by the photoelectric field on subpicosecond timescales. A direct view on the 4*f* electron occupancy of the Eu ions is required to understand the microscopic origin of the transition. Here we probe the 4*f* electron states of $\text{EuNi}_2(\text{Si}_{0.21}\text{Ge}_{0.79})_2$ at the sub-ps timescale after photoexcitation by x-ray absorption spectroscopy across the Eu M_5 -absorption edge. The observed spectral changes due to the excitation indicate a population change of total angular momentum multiplet states $J = 0, 1, 2,$ and 3 of Eu^{3+} and the Eu^{2+} $J = 7/2$ multiplet state caused by an increase in 4*f* electron temperature that results in a 4*f* localization process. This electronic temperature increases combined with fluence-dependent screening accounts for the strongly nonlinear effective valence change. The data allow us to extract a time-dependent determination of an effective temperature of the 4*f* shell, which is also of great relevance in the understanding of metallic systems' properties, such as the ultrafast demagnetization of ferromagnetic rare-earth intermetallic and their all-optical magnetization switching. In addition, our results elucidate the energetics of charge fluctuations in valence-mixed electronic systems, which provide enriched knowledge regarding the role of valence transitions and orbital hybridization for quantum critical phenomena.

DOI: [10.1103/PhysRevResearch.6.023099](https://doi.org/10.1103/PhysRevResearch.6.023099)**I. INTRODUCTION**

Valence transitions of 4*f* electrons and their fluctuations are representative properties of strongly correlated 4*f* electron

systems, comparable to magnetic ordering, unconventional superconductivity, Kondo effect, and non-Fermi-liquid behaviors [1]. However, a detailed description of the underlying processes, even for prototypical systems such as the element Ce, which exhibits a first-order valence transition as a function of pressure [2], remains a challenge. Many valence-transition and -fluctuating materials have fractionally occupied 4*f* states located near the Fermi level (E_F) [1]. Therefore, the hybridization and the Coulomb interaction between localized 4*f* electrons and delocalized 6*s*/5*d* electrons play a major role in realizing the valence transition and its associated fluctuations.

Here, we focus on the Eu intermetallic compound $\text{EuNi}_2(\text{Si}_{0.21}\text{Ge}_{0.79})_2$ to investigate the mechanism of its valence transition. The valence transition between Eu^{2+} ($4f^7$) and Eu^{3+} ($4f^6$) in tetragonal ThCr_2Si_2 -type Eu compounds has been reported as a function of temperature [3–8], magnetic field [9–12], and physical and chemical pressure [3,4,7,8,13–16]. Among them, $\text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2$ series

*Present address: Japan Synchrotron Radiation Research Institute, 1-1-1, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan.

†Present address: Institute of High Energy Physics, Chinese Academy of Sciences, Yuquan Road 19B, Shijingshan District, Beijing 100049, China.

‡Present address: National Institutes for Quantum Science and Technology, 6-6-11-901 Aramaki, Sendai Aoba-ku, Miyagi 980-8579, Japan.

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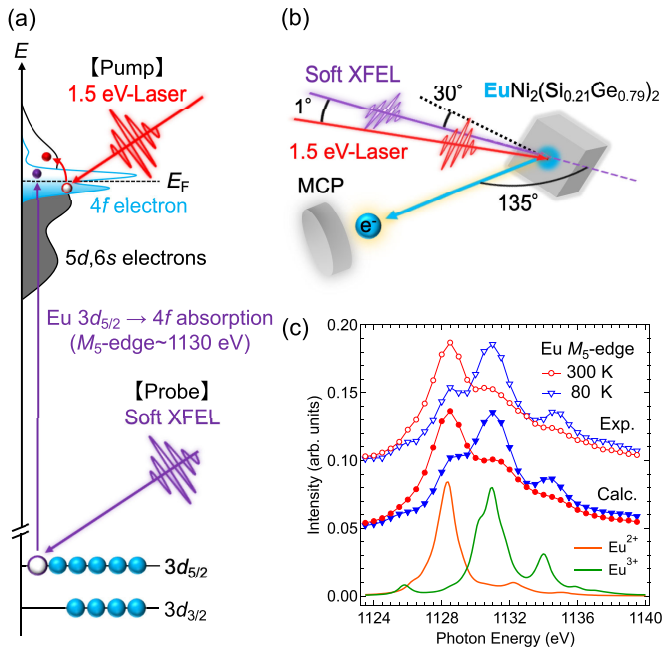


FIG. 1. (a) Schematic of the electronic bands including a core hole of the XAS probe, modifications of the $4f$ states upon laser excitation (red arrows), and $3d_{5/2} \rightarrow 4f$ core-level absorption (M_5 -edge) process (purple arrows). (b) The experimental setup of the tr-XAS. (c) XAS around the Eu M_5 edge at 300 and 80 K (upper spectra) crossing the mixed-valence transition temperature. The middle spectra are the atomic multiplet calculations broadened to match experimental data. The calculated spectral components of the Eu^{2+} and Eu^{3+} free ion spectra are shown at the bottom without convolution with instrumental resolution broadening.

show the temperature-driven valence transition in the range $0.5 \leq x \leq 0.82$ of Ge substitution [3]. The phase transition temperature (T_v) reaches the maximal value of ~ 95 K at around $x = 0.79$, accompanied by the Kondo volume collapse [4]. An interesting aspect is the decreasing Eu valence with increasing temperature, analogous to Ce-based compounds [1,17], in contrast to the increasing lanthanide valence reported for most of the $4f$ systems showing a valence transition, e.g., Yb- and Sm-based compounds [18–23]. The divalent (trivalent) state of the lanthanide valence is localized (delocalized) character due to the electronic repulsion potential of the ion, which results in the large (small) ionic radius. Therefore, the valence transition in $\text{EuNi}_2(\text{Si}_{0.21}\text{Ge}_{0.79})_2$ has been interpreted as a reduction in the hybridization of $4f$ and $6s/5d$ electrons at high temperatures, giving the beneficial opportunity to understand how an electron is localized from the conduction band to the localized $4f$ band.

X-ray absorption spectroscopy (XAS) is a powerful method to investigate the equilibrium electronic state intertwined with the valence transition of lanthanide ions [24]. In addition, by combining it with optical laser excitations, the time-resolved XAS (tr-XAS) can probe nonequilibrium electronic states, currently investigated at x-ray free electron lasers (XFELs) [25–29]. tr-XAS allows us to track hot electrons after photoexcitation that are related to the valence transition. Figure 1(a) shows the schematic of the $6s/5d$ conduction band and the $4f$ band upon optical laser excitation. Since

E_F lies within the $4f$ bands, localized $4f$ electrons can be transferred to/from the conduction band after photoexcitation. Previous tr-XAS at the Eu $3d_{5/2} \rightarrow 4f$ absorption edge (M_5 edge) for $\text{EuNi}_2(\text{Si}_{0.21}\text{Ge}_{0.79})_2$ displayed the photon-induced valence transition and dynamics of both Eu^{2+} and Eu^{3+} ions that were limited by the experimental time resolution of 70 ps [30], which is insufficient to resolve the microscopic pathways of the transition. Recently, a fs x-ray experiment employing radiation from a hard XFEL at the Eu $2p_{3/2} \rightarrow 5d$ absorption edge (L_3 edge) reported a sub-ps electron localization process, which is faster than the thermal expansion of the unit cell occurring within a few picoseconds [31]. The origin of the electron localization has been suggested to be caused by a reduction of the $4f$ hybridization with the conduction bands driven by pure electronic effects, such as screening. However, a clear understanding of the $4f$ electron dynamics at sub-ps timescale remains missing.

Lanthanides containing intermetallics are also of great interest in the field of ultrafast all optical magnetization switching (AOS). In that field, fs pulses of optical excitation can lead to a reversal of the magnetization in, e.g., GdFeCo [32,33]. The excitation is expected to differently affect the magnetization $4f$ and the $3d$ metal ions [34] and it is therefore of more general importance to understand the excited $4f$ electron system and its interaction with $3d$ transition metal ions in intermetallics. A direct view of the ultrafast behavior of $4f$ electrons by probing with fs soft x-ray pulses is therefore of great importance for a better understanding of both AOS and ultrafast electron localization including valence transitions. In this study, we probe the sub-ps $4f$ electronic dynamics of $\text{EuNi}_2(\text{Si}_{0.21}\text{Ge}_{0.79})_2$ using the M_5 -edge tr-XAS which directly probes the $4f$ states and can show how one can directly extract the electronic $4f$ temperature which is of great importance for the ultrafast electron localization as well as basic microscopic quantity in ultrafast magnetization dynamics of lanthanide intermetallics.

II. EXPERIMENTAL CONDITIONS

Polycrystalline $\text{EuNi}_2(\text{Si}_{0.21}\text{Ge}_{0.79})_2$ ingots were grown by the argon-arc melting method [9]. Magnetometry data show T_v to be at ~ 93 K (see Fig. S1 of the Supplemental Material [35]). The sample was mechanically cleaved *in situ* in an ultrahigh vacuum at 150 K to prevent the surface layers from being oxidized.

The tr-XAS measurements were performed at the SSS beamline at the PAL-XFEL in South Korea [36–38]. An 800-nm Ti-sapphire pump laser with a pulse duration of 50 fs in full width of half maximum (FWHM), a repetition rate of 30 Hz, and a focal spot size of $600 \times 600 \mu\text{m}^2$ was used to excite the sample. The XFEL beam had a photon energy of ~ 1130 eV (Eu M_5 edge), a pulse duration of 100 fs in FWHM, a focal spot size of $80 \times 80 \mu\text{m}^2$, and a repetition rate of 30 Hz. The experimental setup is shown in Fig. 1(b). The incidence angle of the XFEL pulse was 30° , and the pump laser was offset by 1° to the x rays, passing through a hole of the last optical mirror before the sample chamber. XAS data with an energy resolution of 0.7 eV were obtained by collecting the emitted electrons with a microchannel plate (MCP) placed in the horizontal plane and at 135° to the XFEL incident

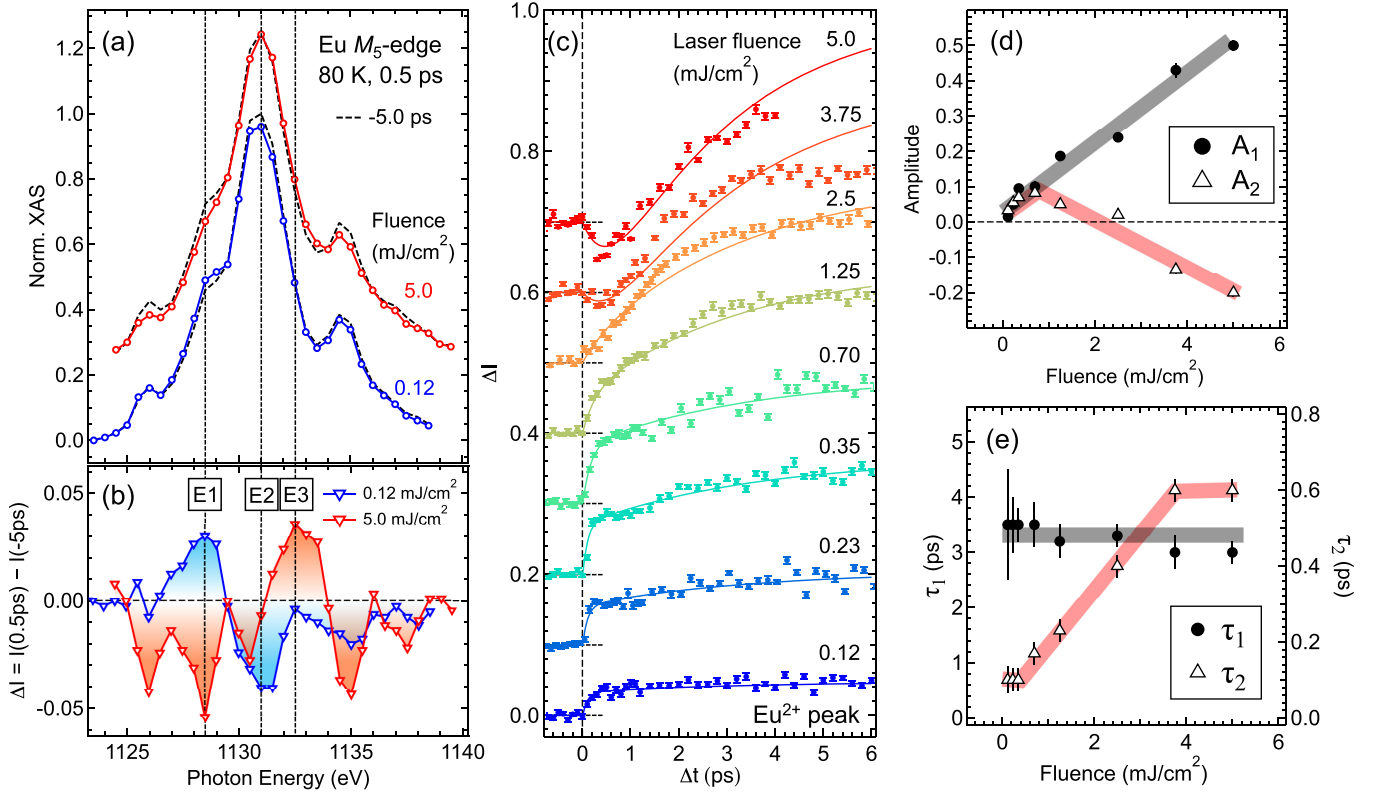


FIG. 2. (a) The Eu M_5 -edge tr-XAS spectra at 80 K under low (0.12 mJ/cm², blue) and high fluences (5.0 mJ/cm², red) with ($\Delta t = 0.5$ ps) and without (black, taken at $\Delta t = -5.0$ ps) laser excitation at early times. (b) XAS spectral intensity changes (ΔI) at 0.5 ps. In panels (a) and (b), the vertical dashed lines denote the photon energies, labeled as E1 = 1128.5 eV, E2 = 1131 eV, and E3 = 1132.5 eV, which are discussed in the main text. (c) Ultrafast ΔI change as a function of Δt for selected fluences at 80 K of the Eu^{2+} peak (E1). The colored solid lines are best fits to two exponential functions. (d),(e) Laser fluence dependence of the amplitude A_i and the recovery time τ_i ($i = 1, 2$). The solid lines guide the eyes.

vector. Delay-time (Δt) scans were taken from -5.0 to 7.0 ps accumulating, at least, 300 shots per step for selected photon energies and each fluence. The data were normalized shot by shot by the incident photon flux (I_0) obtained from a Pt(5 nm)/Si₃N₄(200 nm) film installed upstream of the beamline.

XAS measurements were carried out at 80 and 300 K, temperatures that are clearly below and above T_v , respectively. While the probing depth of the electron yield method is ~ 4 nm [39–42], the excitation depth of the 800-nm laser is about 25 nm for $\text{EuNi}_2(\text{Si}_{0.21}\text{Ge}_{0.79})_2$, which is obtained from optical reflectivity measurements [30,43].

III. Eu VALENCE CHANGES IN EQUILIBRIUM AND NONEQUILIBRIUM

Characterizing the Eu M_5 -edge XAS in equilibrium for temperatures below (80 K) and above T_v (300 K) is a basis for the understanding of the nonequilibrium electronic states [see Fig. 1(c)]. The experimental data are compared with the calculated spectra from multiplet calculations for the ground states of Eu^{2+} and Eu^{3+} free ions [5,30]. In the final state of the M_5 -edge XAS, the interaction between the generated $3d$ core hole and the $4f$ electrons with different $4f$ occupation numbers causes a 2.5-eV energy difference between the Eu^{2+} (1128.5 eV) and Eu^{3+} (1131 eV) main absorption peaks. Therefore, the XAS spectra at 300 and 80 K are dominated by

the Eu^{2+} and Eu^{3+} states, respectively. From the comparison to the calculations, an evaluated effective $4f$ valence (v_{4f}) of 2.36 ± 0.02 at 300 K and 2.71 ± 0.02 at 80 K is obtained, which is in good agreement with the previously reported values [5,6].

Figure 2(a) shows M_5 -edge tr-XAS for the lowest (0.12 mJ/cm²) and highest (5.0 mJ/cm²) fluences at $\Delta t = 0.5$ ps directly probing the excited $4f$ states. The unperturbed XAS data ($\Delta t = -5.0$ ps) are also shown for comparison. The determination of v_{4f} before t_0 results in 2.71 ± 0.02 for both fluences, in perfect agreement with the static measurements confirming the absence of any deterioration of the sample during pump-probe measurements. The photon-induced change in the XAS at 0.5 ps shown in Fig. 2(b) is qualitatively different between low and high fluence. There are some sign changes in the pump effect indicating larger and smaller XAS intensities for XAS, labeled as E1 = 1128.5 eV, E2 = 1131 eV, and E3 = 1132.5 eV, attributed to Eu^{2+} and Eu^{3+} , respectively. These observed pump-probe differences imply a fluence-dependent change in v_{4f} of Eu ions at early times ($\Delta t = 0.5$ ps) after the excitation. A simple spectral analysis from the individual divalent and trivalent spectra as done in Ref. [30] results in v_{4f} of 2.67 ± 0.02 for 0.12 mJ/cm² and 2.77 ± 0.02 for 5.0 mJ/cm², suggesting the increase and decrease of the Eu^{2+} population after photoexcitation at low and high fluence, respectively. This is quantitatively consistent

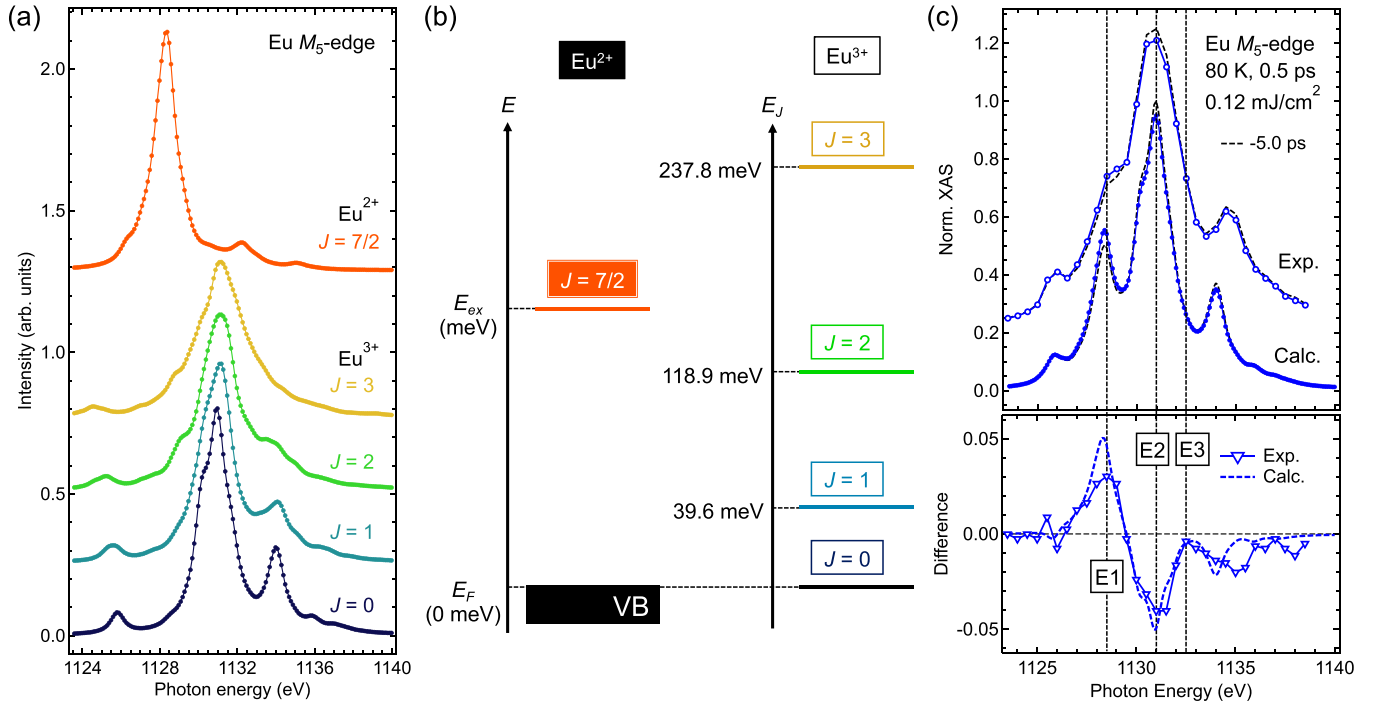


FIG. 3. (a) The atomic multiplet calculations of each J state. (b) Energy level of the ground and excited states for Eu^{2+} and Eu^{3+} free ions. E_{ex} is the energy of Eu^{2+} $J = 7/2$ state from the Fermi level, which is at the Eu^{3+} $J = 0$ state. (c) The experimental and calculated Eu M_5 -edge XAS spectra at 80 K, 0.12 mJ/cm^2 , and $\Delta t = 0.5$ ps. Black dashed curves indicate data without laser excitation taken at $\Delta t = -5.0$ ps (equilibrium). The spectral difference from the equilibrium data is shown in the bottom panel.

with the previous report based on L_3 -edge tr-XAS [31]. As explained in detail later and in the Supplemental Material [35], the anomalous behavior observed in E2 and E3 under high fluences (5.0 mJ/cm^2) originates from the excitation from the $J = 0$ state to higher lying J states of Eu^{3+} , especially the increased occupancy of the $J = 3$ state [Fig. 3(a) and Fig. S6(a) [35]].

By adjusting the photon energy to the Eu^{2+} peak (E1), we directly investigated the time evolution of XAS spectral intensity changes (ΔI) [see Fig. 2(c)]. A stepwise increasing component of the Eu^{2+} peak was observed from the low fluence region (0.12–0.35 mJ/cm^2). Furthermore, a prominent decrease in the Eu^{2+} signal is captured at earlier times through the high fluence region (3.75–5.0 mJ/cm^2). This fluence dependence of the time evolution is analogous to that reported in L_3 -edge tr-XAS [31]. This continuous change in the time evolution as a function of laser fluences can be described by a phenomenological model with different exponential components given by

$$\Delta I(\Delta t) = G(\Delta t) \otimes [(I_1 + I_2)H(\Delta t)], \quad (1)$$

$$I_i = A_i(1 - e^{-\Delta t/\tau_i}), \quad (2)$$

where A_i and τ_i ($i = 1, 2$) denote an amplitude and a time relaxation, respectively. $G(\Delta t)$ is a Gaussian function reflecting the time resolution and $H(\Delta t)$ is the Heaviside function (see Fig. S2). The first component I_1 represents a slow process, possibly the response for the energy transfer from the excited electronic system to the lattice. The second component I_2 should then be associated with the initial charge localization/delocalization process. The obtained A_i and τ_i parameters

are plotted as a function of excitation fluence in Figs. 2(d) and 2(e). The amplitude of the first component shows a linear laser fluence dependence with a relaxation time being almost constant, which is consistent with the previous findings of 70-ps time resolution tr-XAS [30]. The amplitude of the second component is strongly nonlinear with a fluence-dependent increase in the relaxation time and flipping its sign, consistent with the previous findings at the L_3 edge tr-XAS [31]. This directly reveals that the photoexcited $4f$ electronic character changes localized nature to delocalized nature with increasing laser fluence at the subpicosecond timescale. Note that the time evolution of XAS spectral intensity changes at the photon energy of the Eu^{3+} peak (E2) can roughly be reproduced by flipping the sign of $\Delta I(\Delta t)$ in Eq. (1), indicating that $4f$ electrons at both Eu^{2+} and Eu^{3+} ions are simultaneously photoexcited (see Fig. S3).

IV. NONEQUILIBRIUM $4f$ ELECTRONIC STRUCTURE ANALYZED BY THE INTERCONFIGURATIONAL FLUCTUATION MODEL

A significant advantage of M_5 -edge tr-XAS is its direct sensitivity to Eu $4f$ electronic states. Upon increasing laser fluence at the early delay times, the Eu^{3+} main peak at E2 decays and another spectral feature at E3 develops, in addition to the sign change of the Eu^{2+} peak at E1 as shown in Fig. 2(b). It clearly shows that there are competing nonlinear processes such as, e.g., charge localization/delocalization that differently depend on the excitation fluence. Note that these photoinduced processes are sufficiently faster than the volume expansion (~ 3 ps) observed previously [31]. One plausible

mechanism is the electronic temperature increase of the 4f states due to the excitation, which directly leads to an increase in the Eu^{2+} state population. The other possible mechanism is related to the increase of the electronic temperature of the conduction band, which leads to screening that will differently affect the Eu^{2+} and Eu^{3+} states. These mechanisms can compete or coexist, and possibly result in charge localization/delocalization depending on laser fluence, as discussed later.

Let us first state that in a metal, the number of excited electrons in the considered state is not a good description in “equilibrium” as we cannot define an electronic temperature. Here, we use electronic state, e.g., defined by a Dirac distribution, which is now mixed with the Boltzmann statistics and the broadening. Upon photoexcitation, the electron temperature of the conduction band increases, leading to an enhanced hybridization between the conduction (*c*) band and the *f* band. This enhanced hybridization attributes to (1) strengthening the *f-c-f* charge transfer process, (2) inducing an increase of the 4f electron temperature as the 4f level broadening, and (3) raising the occupancy of Eu^{3+} localized 4f excited multiplet states with finite *J*. Since screening can be negligibly small at the lower laser fluence, the photoexcitation behaves similar to thermal excitation [Figs. 2(c) and 2(d)]. Note that lattice expansion takes few ps, as measured by tr-XRD [31], and thus, this localization behavior is driven by the increase in the 4f electronic temperature. However, at very high laser excitations and early times, higher lying *J* multiplets are populated, causing a more trivalent character of the Eu before the phonons cool the electronic system and reversing its effect to get Eu more divalent. A more quantitative description requires an increase in both the Eu^{3+} electron temperature and the energy of the Eu^{2+} localized $J = 7/2$ state upon the laser fluence.

To gain more insight into these scenarios, we consider the excited *J* multiplets of the Eu^{3+} ions within the free-ion approximation that allows us to evaluate the population of the excited states. A multiplet calculation for free Eu^{3+} ions with the different occupations of higher-lying *J* multiplets predicts that the M_5 -edge XAS main peak becomes broader [Fig. 3(a) and Fig. S4], and thus the population can be evaluated from the spectral shape. The electronic 4f temperature can be addressed through the interconfigurational fluctuation (ICF) model, known as a high-temperature model for incoherent thermal charge fluctuations used for rare-earth metals [9,13–15,44–46]. The energy level scheme is shown in Fig. 3(b). E_J is the energy of the Eu^{3+} atomic multiplet states with *J*, neglecting their crystal field splitting [Fig. 3(b)]. E_{ex} is the energy to take one electron out of the conduction band and to put it into the 4f levels converting the Eu valence state from 3+ to 2+. In this model, the populations of the Eu^{2+} and Eu^{3+} states, represented as p_2 and p_3 , respectively, are given by the Boltzmann statistic

$$\begin{aligned} \frac{p_2}{p_3} &= \frac{N_J \exp\left(-\frac{E_{\text{ex}}}{k_B T^*}\right) \Big|_{J=7/2}}{\sum_{J=0}^3 N_J \exp\left(-\frac{E_J}{k_B T^*}\right)} \\ &= \frac{8 \exp\left(-\frac{E_{\text{ex}}}{k_B T^*}\right)}{1 + 3 \exp\left(-\frac{39.6}{k_B T^*}\right) + 5 \exp\left(-\frac{118.9}{k_B T^*}\right) + 7 \exp\left(-\frac{237.8}{k_B T^*}\right)}, \end{aligned} \quad (3)$$

where k_B is the Boltzmann constant. The degeneracy $N_J = 2J + 1$ is adopted as the coefficient of each Boltzmann distribution for the $J = 7/2$ state of Eu^{2+} and $J = 0, 1, 2,$ and 3 states of Eu^{3+} [Fig. 3(a)] and $p_2 + p_3 = 1$. $T^* = \sqrt{T^2 + T_{4f}^2}$ is the effective temperature including the temperature in the system (*T*) and the constant value of the broadening of the 4f state (T_{4f}). In the equilibrium state, by introducing an effective temperature, the broadening of various energy levels of 4f electronic states due to quantum mechanical hybridization, such as orbital hybridization and electron-lattice interactions, can be accommodated. In the photoexcited nonequilibrium state, since the 0.2-ps timescale of the broadening of conduction band including Eu 5*d* states [31] is faster than 0.5 ps of Eu 4f states, rather than *T* alone, T^* is a better parameter to describe the temperature of 4f states, which could be different than that of the conduction band [47]. Here, E_{ex} and T^* are the tuning parameters to reproduce the XAS data and ν_{4f} is given by $\nu_{4f} = 3 - p_2$. The excited Eu^{3+} spectra for a given electronic temperature T^* were obtained by summing the XAS spectra of each *J* state, shown in Fig. 3(a), multiplied by their population. Figure 3(c) shows the experimental M_5 -edge tr-XAS for 0.12 mJ/cm² at 80 K and $\Delta t = 0.5$ ps together with equilibrium data for comparison ($\Delta t = 5.0$ ps) as well as the calculated tr-XAS based on the ICF model. Spectral differences between excited and ground states for experimental and calculated data sets are shown in the bottom panel of Fig. 3(c). The calculated spectra obtained by the ICF model reproduce well the experimental data. As referred from the previous L_3 -edge XAS [9], E_{ex} and T^* in the equilibrium XAS data are estimated to be 48 meV and 203 K at 80 K and 26.4 meV and 353.5 K at 300 K, respectively [Fig. S5]. Furthermore, it confirms that the calculated $\nu_{4f} = 2.71$ matches to our static M_5 -edge XAS result at $T = 80$ K [Fig. 1(c)]. For the excited state at $\Delta t = 0.5$ ps, T^* is estimated to be 222 K when fixing E_{ex} to 48 meV.

Figures 4(a) and 4(b) show the experimental and calculated data of the tr-XAS and their spectral deviations from the equilibrium data for selected laser fluences at $\Delta t = 0.5$ ps and $T = 80$ K, respectively. The experimental data are well described by a fit to the ICF model with the following restrictions on T^* and E_{ex} . Since the initial photoabsorption process heats only the electronic structure, the temperature T^* is assumed to be proportional to the laser fluence. Its slope is derived from the experimental data for the 0.12 mJ/cm² at $\Delta t = 5.0$ ps (equilibrium) and 0.5 ps (nonequilibrium). E_{ex} is freely tuned to reproduce the experimental data. The occupation of each multiplet state plotted as a function of laser fluence in Fig. S6(a) indicates strongly nonlinear behavior, except for the Eu^{3+} $J = 2$ state. E_{ex} is found to increase approximately linear with fluence except for low fluences, as shown in Fig. S6(b). Note that the increase in E_{ex} at early times ($\Delta t = 0.5$ ps) is not an absolute energy increase of the Eu^{2+} states but is in respect to the changes of the Eu^{3+} states population. The nonlinear effect on the valence change, as obtained in the time traces at 0.5 ps, is a consequence of E_{ex} being constant at small fluences and the intrinsic nonlinear behavior of the population in the Boltzmann statistics.

To better visualize the origin of the sign change in the electron localization/delocalization as a function of fluence

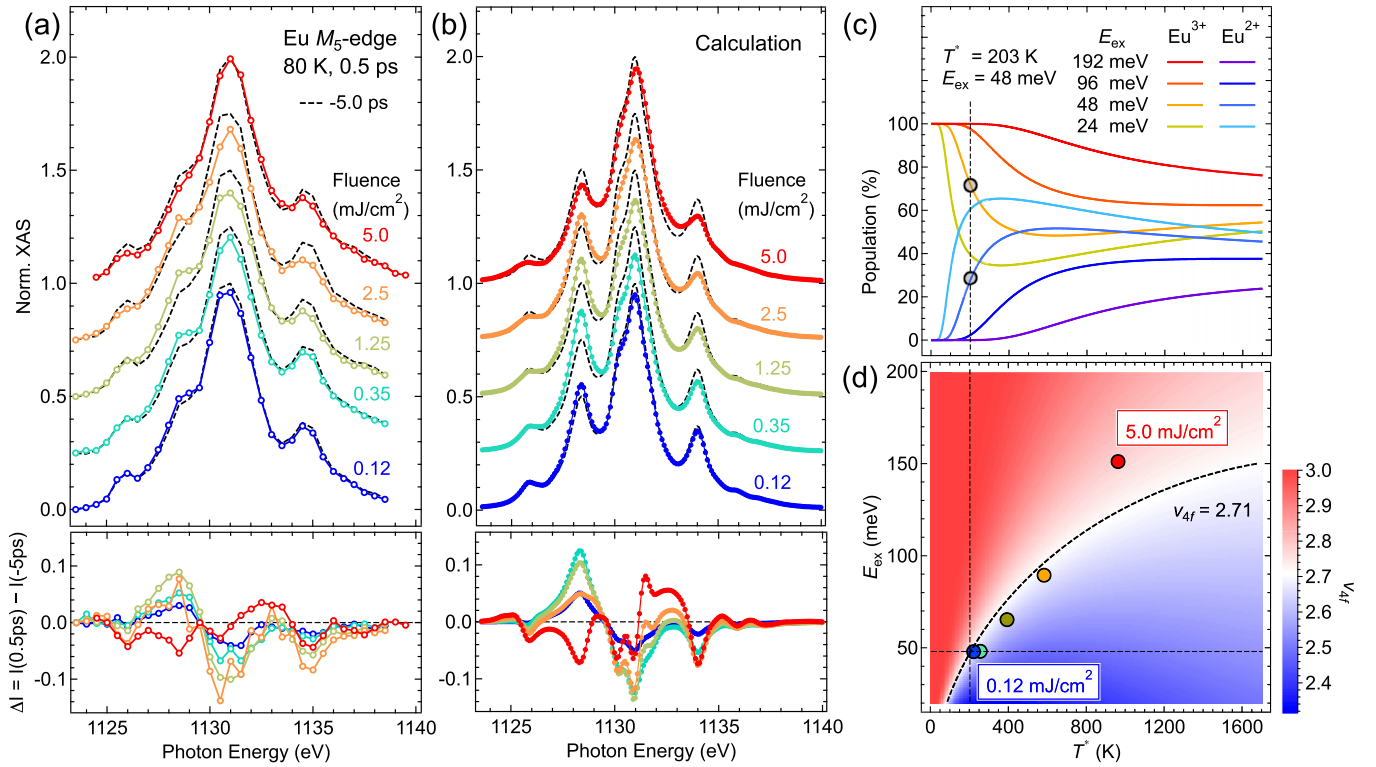


FIG. 4. The M_5 -edge XAS and ΔI spectra for selected fluences at 80 K and $\Delta t = 0.5$ ps, together with equilibrium data taken at $\Delta t = -5.0$ ps. (b) The calculated XAS and their difference from equilibrium spectrum reproduces well the experimental results. (c) Calculated Eu^{2+} and Eu^{3+} populations at different E_{ex} as a function of T^* . The vertical black dashed line with circle marks approximately the equilibrium case (80 K). (d) The $T^* - E_{\text{ex}}$ mapping of the Eu valence. The circles denote the obtained values for each fluence from spectral fits based on the ICF model. The curved dashed line corresponds to the Eu valence of 2.71. Horizontal line cuts at fixed $E_{\text{ex}} = 24, 48, 96, 192$ meV, denoting nonlinear Eu valence change as a function of T^* , are shown in Fig. S7.

at 0.5 ps, we plot the population changes of the Eu^{2+} and Eu^{3+} while keeping E_{ex} fixed in Fig. 4(c). This allows us to qualitatively understand the time traces taken at the main XAS peak of the Eu^{2+} (E1). Figure 4(d) shows the $T^* - E_{\text{ex}}$ mapping of v_{4f} . At low fluence, the increase in T^* just leads to a population increase of the divalent state. For high fluence, the ultrafast increase in T^* can lead to an increase of the valence state; however, as the electronic temperature cools due to energy transfer to the lattice, it leads again to reduced E_{ex} at later times and the population of the Eu^{2+} increases again.

V. DISCUSSION: ULTRAFAST $4f$ LOCALIZATION AND RELATED MAGNETIC PHENOMENA

These findings allow us to draw a semiquantitative picture on the valence change and its mechanism of the photoinduced valence transition. After the initial excitation of the electronic structure, the energy transfers in approximately 3 ps to the optical phonons and later to acoustic modes, as found previously by ultrafast x-ray diffraction [31]. The initial excitation does not only inject energy into the different $4f$ states but also increases the electron mobility (electron temperature of the conduction band) leading to screening effects, which is responsible for a change of E_{ex} . Attosecond experiments have previously shown that screening leads to an electron localization in Cu metal [48]. In our case, however, the turnover from

charge localization to delocalization for increasing fluence is intrinsically contained in the population changes by solely increasing the effective temperature in the ICF model alone. On the other hand, the ICF model is rather limited, as the $4f$ bandwidth, which contains the important hybridization between conduction electrons and localized $4f$ states, is only described by its contribution to the effective temperature. A quantitative understanding of the intrinsic effect of screening and effective $4f$ temperature for valence transition requires a description that includes hybridization and interaction of conduction electrons with localized $4f$ and delocalized $5d$ Eu states more adequately, which is not possible in the phenomenological ICF model used here. However, it shows that the spectral shape changes allow a quantitative determination of the $4f$ electron temperature. In general, this is of great interest in studies on ultrafast magnetization dynamics, in particular for magnetic $4f$ materials such as those showing all-optical magnetization switching, e.g., GdFeCo [32,33,47,49,50]. A determination of the electronic temperature of the $4f$ electron systems in $4f$ intermetallics materials or multilayers will be of great importance to understand the demagnetization processes as well as intersite spin processes [51] believed to be relevant for ultrafast magnetization dynamics. In addition, it has been recently shown that excited $4f$ multiplet (orbital) states are important for the magnetization dynamics of Tb metal [52].

VI. CONCLUSION

The time-resolved Eu M_5 -edge XAS quantifies the valence change induced by an optical excitation in a valence fluctuating $\text{EuNi}_2(\text{Ge}/\text{Si})_2$ intermetallic. The approach of direct detection of the 4f states through spectral changes allows addressing the effective electronic temperature of the 4f states through the interconfigurational fluctuation model. The obtained results support the view that an ultrafast temperature increase of the 4f system is responsible for initial charge localization in the 4f states at low fluences, which brings a novel spin on the physics of 4f valence fluctuations. For higher fluences, screening effects must be considered. Beyond valence fluctuation/transition physics, the determination of the 4f electron temperature by means of the XAS method will also be of significant interest to mixed 4f-3d systems that show ultrafast demagnetization or all-optical magnetization switching.

ACKNOWLEDGMENTS

We thank H. Watanabe and Y. Yokoyama for the fruitful discussions. The experiments were performed at SSS end station of PAL-XFEL (Proposal No. 2019–2nd-SSS-014) funded by the Ministry of Science and ICT of Korea. This work was supported by MEXT Quantum Leap Flagship Program (MEXT Q-LEAP) Grant No. JPMXS0118068681. This work also was supported by JSPS KAKENHI Grant-in-Aid (No. 19H05824 and No. 21H03739). H.U. was supported by the National Centers of Competence in Research in Molecular Ultrafast Science and Technology (NCCR MUST Grant No. 51NF40-183615) from the Swiss National Science Foundation and from the European Union's Horizon 2020 research and innovation program under Marie Skłodowska-Curie Grant Agreement No. 801459–FP-RESOMUS. Y.Z. was supported by the JSPS KAKENHI Grant No. 17F17327.

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