

# Site-specific valence fluctuations in $\text{Eu}_3\text{Pd}_{20}\text{Ge}_6$ studied via Mössbauer and x-ray absorption spectroscopies

Satoshi Tsutsui,<sup>1,\*</sup> Masaichiro Mizumaki,<sup>1</sup> Yoshio Kobayashi,<sup>2</sup> Jiro Kitagawa,<sup>3</sup> and Toshiro Takabatake<sup>3</sup>

<sup>1</sup>Japan Synchrotron Radiation Research Institute, SPring-8, Sayo, Hyogo 679-5198, Japan

<sup>2</sup>Nishina Center for Accelerator Based Science, RIKEN, Wako, Saitama 351-0198, Japan

<sup>3</sup>Graduate School of Advanced Sciences of Matter, Hiroshima University, Higashi-Hiroshima, Hiroshima 739-8530, Japan

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We have employed a combination of x-ray absorption spectroscopy (XAS) and  $^{151}\text{Eu}$  Mössbauer spectroscopy (MS) to elucidate the Eu valence-fluctuating states in  $\text{Eu}_3\text{Pd}_{20}\text{Ge}_6$  with two nonequivalent sites  $4a$  and  $8c$ . The XAS spectra show two components of  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  states, the spectral weights of which depend on temperature and the average valence becomes a constant value of  $\sim 2.85$  below 150 K. The MS spectra, however, show three components. Our analysis revealed that Eu ions at the  $4a$  site are in an intermediate state with a characteristic frequency of a few hundred MHz, while the valence fluctuation of the Eu ions at the  $8c$  site has a much lower frequency.

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## I. INTRODUCTION

Some Ce, Eu, Sm, and Yb compounds are known to be valence-fluctuating compounds.<sup>1</sup> In these compounds, the ground state in one of the valence states is magnetic and that in the other is nonmagnetic. Therefore, magnetic-susceptibility measurement provides a rough estimation of the average valence. In addition, the ionic radius depends on the valence state even in the same element. Therefore, another estimation of the average valence is given by the degree of deviation from the lanthanide contraction of the lattice constant in a series of rare-earth compounds. Since rare-earth atoms in most valence-fluctuation systems investigated previously occupy one site,<sup>2–19</sup> the analysis of the magnetic susceptibility and the investigation of the lattice constant are useful in estimating their valence states at rare-earth sites. These approaches apply to the investigation of the physical properties of the valence-fluctuating compound  $\text{SmB}_6$ , for example.<sup>2–6</sup> However, these estimations fail in a compound with multiple sites for rare-earth atoms. It is also difficult to estimate the fluctuation time for each site.

Eu compounds are a suitable system for investigating valence fluctuation. Here, we briefly review studies of Eu valence-fluctuation systems. Among them, systematic studies associated with structural and electronic investigations were carried out in the series of  $\text{EuT}_2\text{X}_2$  ( $T$ : transition metal,  $X$ : Si or Ge), for example.<sup>7–16</sup> Temperature dependences of the average valence state estimated by both x-ray absorption spectroscopy (XAS) and Mössbauer spectroscopy (MS) are consistent with each other.<sup>7</sup> In addition, the temperature dependence of the lattice parameters in these compounds is found at the same temperature at which the average valence state is changed, reflecting the difference in the  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  ionic radii.<sup>8,9</sup> Furthermore, the temperatures where the measured magnetic-susceptibility curves deviate from theoretical ones of  $\text{Eu}^{2+}$  or  $\text{Eu}^{3+}$  free ions agree reasonably well with the results of XAS and MS measurements.<sup>7</sup> To be exact, however, the magnetic susceptibility is affected by the magnetic excited states of the nonmagnetic  $\text{Eu}^{3+}$  state with no total angular momentum. This fact makes it difficult to derive the valence state in general.

Among valence-fluctuation compounds, Eu compounds have an advantage for the quantitative analysis of the valence and frequency because both XAS and  $^{151}\text{Eu}$  MS are applicable. One can obtain information on the valence state from the shift of the XAS and  $^{151}\text{Eu}$  MS spectra. The energy shift of the absorption edge in the XAS spectra corresponds to the valence state of the specific elements. The magnitude of the integrated intensity in the spectra provides the ratio of each valence states. The time window of XAS is  $\sim 10^{-16}$  s ascribed to the core hole lifetime.<sup>20,21</sup> On the other hand,  $^{151}\text{Eu}$  MS provides the local electronic state such as valence state and magnetic interaction. The isomer shift (IS), a useful parameter for investigating the valence state, in  $^{151}\text{Eu}$  MS is different between divalent and trivalent cases. The absorption intensity approximately reflects the volume fraction of each site. The typical time scale of  $^{151}\text{Eu}$  MS is from  $\sim 10^{-8}$  and  $\sim 10^{-9}$  s.<sup>22–24</sup>

$\text{Eu}_3\text{Pd}_{20}\text{Ge}_6$  is a cubic cage-structured compound with two nonequivalent Eu sites.<sup>25</sup> This compound is a member of the series of  $R_3\text{Pd}_{20}\text{X}_6$  ( $R$ : rare-earth or actinide,  $X$ : Ge and Si), whose structure has the space group of  $Fm\bar{3}m$ .<sup>25–27</sup> As illustrated in Fig. 1, the Eu atoms in the  $4a$  site are surrounded by six Ge at the  $24e$  site and 12 Pd atoms at the  $48h$  site, and those in the  $8c$  site with 16 Pd atoms, four of them at the  $32f$  site and 12 at the  $48h$  site. The intermediate-

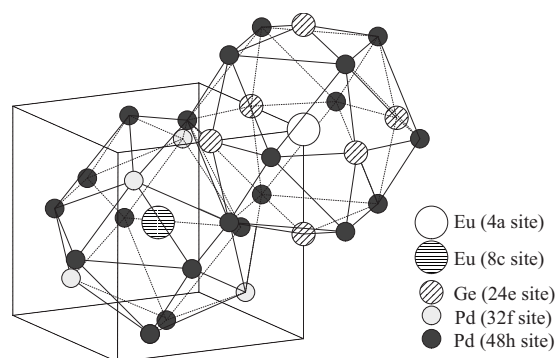


FIG. 1. Ligands of  $4a$  and  $8c$  sites of Eu ions in  $\text{Eu}_3\text{Pd}_{20}\text{Ge}_6$ .

valence state of this compound was first indicated by the temperature dependence of the magnetic susceptibility and the rare-earth dependence of the lattice constant based on the lanthanide contraction.<sup>25</sup> The magnetic-susceptibility measurement suggests the presence of a slow Eu valence fluctuation in  $\text{Eu}_3\text{Pd}_{20}\text{Ge}_6$  even at low temperatures, judging from the deviation of the magnetic-susceptibility curve from the theoretical  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  curves. However, it has not yet been clarified which Eu site is in a valence-fluctuating state. The family of  $R_3\text{Pd}_{20}\text{Ge}_6$  shows attractive physical properties. For example, magnetic ordering and/or quadrupolar ordering occurs independently at  $4a$  and  $8c$  sites in  $\text{Ce}_3\text{Pd}_{20}\text{Ge}_6$  and  $\text{U}_3\text{Pd}_{20}\text{Si}_6$ .<sup>26,27</sup> A recent  $^{139}\text{La}$  NMR study of  $\text{La}_3\text{Pd}_{20}\text{X}_6$  ( $X=\text{Si}, \text{Ge}$ ) indicated that the electronic states and lattice dynamics are different between  $4a$  and  $8c$  sites.<sup>28</sup> The results of those experiments suggested distinct electronic states for the two sites.

Site-specific valence fluctuations were reported in some compounds.<sup>29-31</sup> These compounds certainly show mixed-valence states at their rare-earth sites with multiple valence-fluctuating sites. The rare-earth valence states are determined by the magnetic-susceptibility and XAS measurements. However, no experimental determinations of the valence states were performed at each site in these compounds. Keeping this in mind, we carried out Eu  $L_3$ -edge XAS and  $^{151}\text{Eu}$  MS. As a result, we succeeded in the observation of the first example of site-specific valence fluctuations with estimated valence state and fluctuation frequency at each Eu site in this compound.

## II. EXPERIMENTAL RESULTS

### A. Sample preparation

A polycrystalline sample of  $\text{Eu}_3\text{Pd}_{20}\text{Ge}_6$  was prepared by arc melting the constituent elements, as reported in Ref. 25. The arc-melted sample was annealed in an evacuated quartz tube at 1073 K for 1 week. The obtained sample was confirmed as a single-phase sample by powder x-ray diffraction analysis at room temperature. The sample was crushed into powder, which was used for the XAS and  $^{151}\text{Eu}$  MS measurements.

### B. X-ray absorption spectroscopy

XAS spectra at the Eu  $L_3$ -edge were measured at BL01B1 of SPring-8 in Japan. The incident x-ray was monochromatized by Si (1 1 1) double crystal monochromator and higher-order harmonics were eliminated by a Si mirror. The energy resolution of the beamline optics is approximately 1 eV at the energy of the Eu  $L_3$ -edge, 6982 eV. The x-ray energy was calibrated by the XAS spectrum of the purely trivalent Eu state in  $\text{Eu}_2\text{O}_3$  at 300 K. The measurements were carried out by a transmission method. The XAS spectra were measured at various temperatures from 10 to 300 K.

Figure 2 shows XAS spectra of  $\text{Eu}_3\text{Pd}_{20}\text{Ge}_6$  at 15, 140, and 300 K. The spectra consist of two well-separated peaks, suggesting the coexistence of the divalent and trivalent states. The peak energies are 6975 and 6982 eV, typical values in  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  valence states, respectively. The spectra

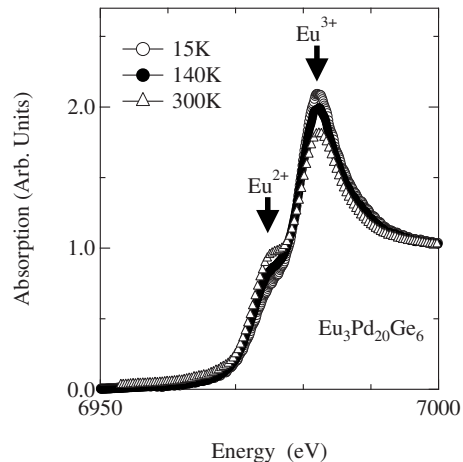


FIG. 2. Eu  $L_3$ -edge XAS spectra of  $\text{Eu}_3\text{Pd}_{20}\text{Ge}_6$  at 15, 140, and 300 K.

show significant temperature dependence. Since the ratio of the peak intensity corresponds to that of the valence states, the observed temperature dependence suggests that the average valence changes as temperature decreases. The determination of the average valence was carried out in the same way as described in Ref. 32. The temperature dependence of the average Eu valence is shown in Fig. 3. The average valence changes linearly above  $\sim 150$  K, whereas it is constant below  $\sim 150$  K. The average valence of the Eu ions is 2.84 below  $\sim 150$  K. This temperature dependence of the  $4f$ -electron number is similar to that in the valence-fluctuation compound  $\text{SmOs}_4\text{Sb}_{12}$ .<sup>32</sup> This behavior seems to be common in valence-fluctuation systems.<sup>6,32</sup>

### C. $^{151}\text{Eu}$ Mössbauer spectroscopy

$^{151}\text{Eu}$  Mössbauer spectroscopy was carried out by the transmission method with  $^{151}\text{SmF}_3$  source of 100 mCi. The Doppler velocity is calibrated by the  $^{57}\text{Fe}$  spectrum of  $\alpha\text{-Fe}$  at 295 K. The zero velocity is determined by the isomer-shift

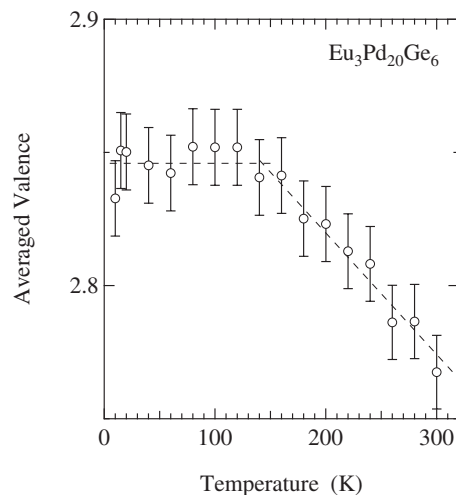


FIG. 3. Temperature dependence of the average valence in  $\text{Eu}_3\text{Pd}_{20}\text{Ge}_6$  determined from the Eu  $L_3$ -edge XAS spectra.

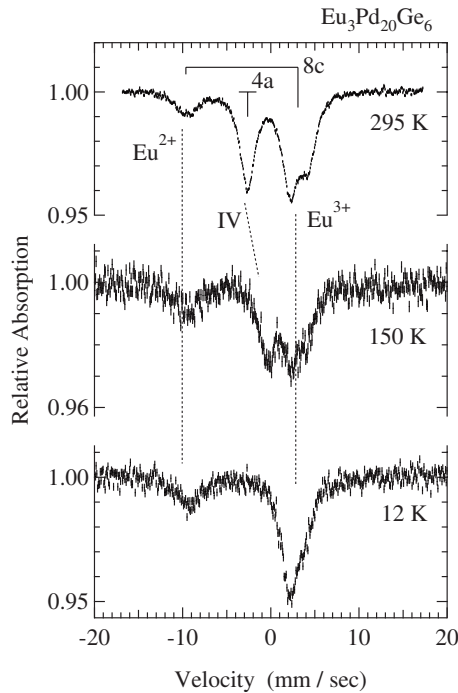


FIG. 4.  $^{151}\text{Eu}$  Mössbauer spectra of  $\text{Eu}_3\text{Pd}_{20}\text{Ge}_6$  at 12, 150, and 295 K.

value of  $\text{EuF}_3$ . The  $^{151}\text{Eu}$  MS spectra were measured at various constant temperatures between 12 and 295 K.

$^{151}\text{Eu}$  MS spectra of  $\text{Eu}_3\text{Pd}_{20}\text{Ge}_6$  at three selected temperatures are presented in Fig. 4. The spectrum consists of three components at 295 K. The isomer shift of the component at the highest velocity is  $3.1 \pm 0.1$  mm/s (shown as  $\text{Eu}^{3+}$ ), a typical value in trivalent states, and that at the lowest velocity is  $-9.6 \pm 0.3$  mm/s (shown as  $\text{Eu}^{2+}$ ), a typical value in divalent states. The isomer shift of the other component suggests an intermediate-valence (IV) state (shown as IV). The evaluation of the valence state of the IV site is rather difficult because the isomer shift is sensitive to not only the valence state but also the coordination number and/or hybridization with ligand atoms. If we assume that the isomer shifts at the  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  sites in this compound are standard values of the divalent and trivalent states in this system, respectively, we can estimate the valence state of the IV site as  $2.55 \pm 0.02$ . Since the relative absorption in the MS reflects the volume fraction of each site, the averaged valence is obtained as  $2.75 \pm 0.15$  by  $^{151}\text{Eu}$  MS spectrum at 295 K, which agrees with that obtained by the XAS,  $2.76 \pm 0.02$ . Although no IV signal was observed in the XAS spectra, a result of  $^{151}\text{Eu}$  MS means that the Eu valence state at either site is indeed fluctuating in time between the two time scale of  $\sim 10^{-16}$  s for XAS and from  $10^{-8}$  to  $10^{-9}$  s for MS.

The observation of three components contradicts the two crystallographic sites for Eu atoms in  $\text{Eu}_3\text{Pd}_{20}\text{Ge}_6$ .<sup>25</sup> This means that the spectrum of both sites or one of the two sites consists of more than one component. Since the spectral weight corresponds to the volume fraction of each electronic state, we assign each component using the ratio of the spectral weight. The normalized ratio of the three sites is

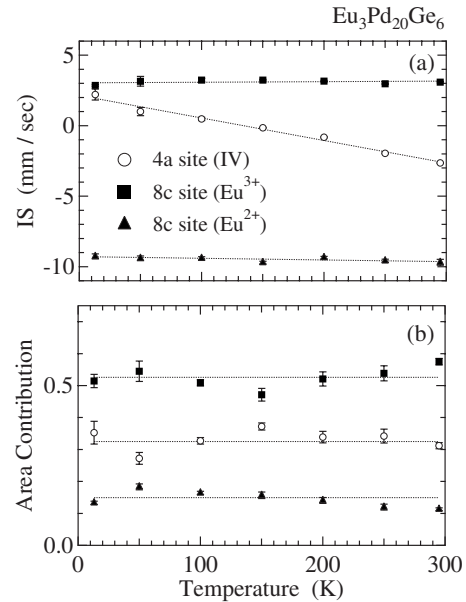


FIG. 5. (a) Temperature dependence of the IS at each component. The dotted lines are least-square fits, assuming a linear temperature dependence of the IS values. (b) Temperature dependence of the spectral weight at each component. The dotted lines are a fitted one, assuming linear temperature dependence of the component ratio.

$(0.12 \pm 0.09) : (0.31 \pm 0.07) : (0.57 \pm 0.07)$  from the lower velocity side to the higher velocity one. If the  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  components are recognized as a set of one Eu site and the IV component is that of the other Eu site, the spectral weight ratio of the former to the latter is  $2.2 \pm 0.3$ . This number agrees with the ratio of the number of atoms for the 4a and 8c sites, 1: 2. Therefore, we assign the spectrum at the 4a site to the IV component and the spectrum at the 8c site consists of the  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  components.

The  $^{151}\text{Eu}$  Mössbauer spectra show significant temperature dependence between 295 and 12 K, as shown in Fig. 4. The isomer shift at the component assigned to the 4a site changed as a function of temperature, whereas that assigned to the 8c site does not. The 4a site component shows significant temperature dependence. Its valence state is an IV state at most of the measured temperatures and is chosen to a pure  $\text{Eu}^{3+}$  one at the lowest temperature. This is similar to the previous result for the valence state compound  $\text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2$ .<sup>7</sup> The component at the 4a site is merged into the trivalent contribution of the 8c site at 12 K.

The temperature dependences of the isomer shift of the three components are shown in Fig. 5(a). The value shows significant temperature dependence, whereas those of the 8c sites are essentially temperature independent. On the other hand, the spectral weights of the three components are constant, as shown in Fig. 5(b). At all the temperatures, the average ratio of the 4a and 8c sites remains a constant 1:2. This indicates that the Debye temperature is the same at each component. In general, the temperature dependence of the integrated intensity in Mössbauer spectra obeys Debye model. If the temperature dependence of the intensity at a component differs from that for other components, this sug-

gests that the Debye temperature is different among them. In other words, the spectral weight shows significant temperature dependence. Since the spectral weight at each component is constant in the present case, however, the Debye temperature is independent of the electronic sites. In addition, the average valence state at  $8c$  site is independent of temperature. These Mössbauer parameters, isomer shifts, and spectral weights demonstrate that only the Eu valence state at the  $4a$  site contributes to the temperature dependence of the average Eu valence obtained by the Eu  $L_3$ -edge XAS. Moreover, a result similar to that in the  $4a$  site of  $\text{Eu}_3\text{Pd}_{20}\text{Ge}_6$  was reported in  $\text{SmB}_6$ .<sup>2-5</sup> In the  $^{149}\text{Sm}$  MS case, the difference of isomer shifts between the divalent and trivalent states, which is comparable to the natural linewidth of  $^{149}\text{Sm}$  Mössbauer resonance, is small for discussing the frequency of the Sm valence fluctuation precisely. Nevertheless, the observation of the two peaks in XAS spectra and an intermediate isomer shift in  $^{149}\text{Sm}$  MS spectra suggest that the valence fluctuation is realized in  $\text{SmB}_6$ .

### III. DISCUSSION

The  $^{151}\text{Eu}$  MS measurements agree qualitatively with the Eu  $L_3$ -edge XAS measurements in the present work. Average Eu valence is an intermediate state between divalent and trivalent states and approaches to a trivalent state with decrease in temperature in both measurements. However, the average valence obtained by the Mössbauer measurements disagrees quantitatively with that discussed by the XAS measurements. The IS value of the  $4a$  site obtained by the MS shows temperature dependence between 12 and 300 K, whereas the average valence obtained by the XAS measurements is constant below about 150 K. The temperature dependence of the IS value means that the average Eu valence obtained by the MS measurements is changed more gradually by the decrease in temperature. This is mainly caused by the difference in the time window between the XAS and  $^{151}\text{Eu}$  Mössbauer measurements because the time window of the XAS ( $\sim 10^{-16}$  s) is much shorter than that of the  $^{151}\text{Eu}$  MS ( $10^{-8}$ – $10^{-9}$  s). As was mentioned above, the number of components in the Mössbauer spectra is inconsistent with that of the crystallographic sites in  $\text{Eu}_3\text{Pd}_{20}\text{Ge}_6$ . In addition, the IV component is observed in the  $^{151}\text{Eu}$  Mössbauer spectra of this compound. These findings indicate that the Eu atoms belonging to both  $4a$  and  $8c$  sites show valence fluctuation. The observation of the IV component indicates that the frequency of the valence fluctuation is close to the time window of the  $^{151}\text{Eu}$  Mössbauer effect, a few hundred MHz; the frequency of the valence fluctuation at the  $8c$  site is less than 100 MHz, slower than that at the  $4a$  site. Once the Mössbauer parameters at the  $4a$  site are determined, the frequency of the valence could be estimated more precisely by the spectral analyses. In the present case, however, the determination of the precise Mössbauer parameters is difficult at any temperature because of a small nuclear quadrupole interaction and an unknown isomer shift of the divalent and triva-

alent states at the  $4a$  site. The former reason is a result of the nature of the  $^{151}\text{Eu}$  nucleus, which has small nuclear quadrupole moments in both excited and ground states; the latter is experimentally difficult to determine. The isomer shift is determined from the center of mass in the spectra. This means that the valence states at both  $4a$  and  $8c$  sites are IV, which is characteristic of valence-fluctuation systems.

We recall here the crystallographic studies and band calculation of the isostructural compounds  $R_3\text{Pd}_{20}\text{Ge}_6$  ( $R = \text{La}, \text{Ce}$ ).<sup>26,33,34</sup> It has been reported that the  $4d$  electrons of the Pd atoms located at the  $48h$  site are crucial in realizing the different electronic states between the  $4a$  and  $8c$  sites in  $\text{Ce}_3\text{Pd}_{20}\text{Ge}_6$ . The Pd atoms at the  $48h$  site are shared by Ce atoms at both  $4a$  and  $8c$  sites in  $\text{Ce}_3\text{Pd}_{20}\text{Ge}_6$ , where the bond length between the  $4a$  and  $48h$  sites is shorter than that between  $8c$  and  $48h$  sites.<sup>26,33</sup> The Pd atoms at the  $32f$  sites are the closest to the Ce atoms at the  $8c$  site in this compound. These structural facts suggest that  $4f$ - $4d$  hybridizations are realized between the  $4a$  and  $48h$  sites and between the  $8c$  and  $32f$  sites. On the other hand, the band calculation of  $\text{La}_3\text{Pd}_{20}\text{Ge}_6$  suggests that the  $4d$  bands of the Pd atoms at the  $48h$  site are wider than those at the  $32f$  site and that the mixing with  $4d$  electrons at the  $4a$  site is stronger than that at the  $8c$  site.<sup>34</sup> Note that valence-fluctuation behaviors are realized under a strong hybridization between  $4f$  and conduction electrons. The present work on  $\text{Eu}_3\text{Pd}_{20}\text{Ge}_6$  clarifies that the hybridization of the  $4d$  electrons at the  $48h$  site with the  $4f$  electrons plays an important role, at least in determining the frequency of the valence fluctuation in  $\text{Eu}_3\text{Pd}_{20}\text{Ge}_6$ .

### IV. CONCLUSION

We have succeeded in distinguishing the frequency range of the Eu valence fluctuation at the  $4a$  site from that at the  $8c$  site, as well as determining the Eu valence states at these sites in  $\text{Eu}_3\text{Pd}_{20}\text{Ge}_6$ . The combination of XAS and MS experiments allowed us to conclude that the Eu valence states at both sites fluctuate at different frequencies; one with a few hundred MHz and the other with a much lower frequency. The quantitative inconsistency of the temperature dependence of the average Eu valence between XAS and MS measurements is caused by the time window difference between these measurements.

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\*satoshi@spring8.or.jp

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