Eu charge and atomic dynamics in Eu$_3$Pd$_{20}$Ge$_6$ investigated by $^{151}$Eu Mössbauer effect

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Abstract. We investigated the Eu charge and atomic dynamics in Eu$_3$Pd$_{20}$Ge$_6$ by conventional $^{151}$Eu Mössbauer spectroscopy and $^{151}$Eu nuclear resonant inelastic scattering. The results of $^{151}$Eu Mössbauer spectroscopy indicate the presence of the Eu valence fluctuation both at the 4a and 8c site with different frequency. The $^{151}$Eu nuclear resonant inelastic scattering spectra differ from the previous results of filled skutterudites.

1. Introduction
Much attention to the potential of thermoelectric materials has been paid in cage-structured compounds. One of the reasons is the expectation of the presence of an Einstein-like phonon mode to reduce thermal conductivity. On the other hand, the cage-structured compounds are also interesting because of the aspects of strongly correlated electronic systems in rare-earth and actinide compounds. The compounds into whose cage a rare-earth atom is inserted provide the opportunity for the hybridization between f-electrons and conduction electrons, because rare-earth ions are surrounded by many conduction electrons.

The series of R$_3$Pd$_{20}$X$_6$ (R: rare-earth and actinide, X: Si or Ge) compounds is one of the interesting cage structured compounds. Since the crystal structure contains a $Fm\overline{3}m$ symmetry, this series of compounds has two non-equivalent rare-earth sites: the 4a and 8c sites. The rare-earth ions at the 4a site are surrounded by six Ge atoms and twelve Pd atoms and those at the 8c site are surrounded by sixteen Pd atoms. Among the Pd atoms surrounding the rare-earth atoms, sixteen Pd atoms occupying at the 48 h site are shared by rare-earth atoms at both sites.

Eu$_3$Pd$_{20}$Ge$_6$ is a valence fluctuating compound [1]. The deviation of the linear correlation of the lattice constant from the line estimated by lanthanide contraction in the series of R$_3$Pd$_{20}$Ge$_6$ suggests that the Eu valence state is no longer a pure Eu$^{3+}$ one. In addition, the deviation of the magnetic
susceptibility from the calculation for both free Eu$^{3+}$ and Eu$^{2+}$ suggests that the Eu valence state is fluctuating. These facts infer that Eu$_3$Pd$_{20}$Ge$_6$ is a valence fluctuating compound. We have carried out $^{151}$Eu Mössbauer spectroscopy to investigate the Eu valence states in this compound from the microscopic point of view. The obtained spectrum at room temperature demonstrates that the Eu valence states are different between two crystallographic Eu sites.

Eu$_3$Pd$_{20}$Ge$_6$ also shows lower thermal conductivity than some heavy fermion or valence fluctuating compounds [1-3]. This behaviour is characteristic of cage-structured compounds such as filled skutterudites and type-I clathrates [4-6]. However, the reduction of the thermal conductivity in Eu$_3$Pd$_{20}$Ge$_6$ is smaller than those of filled skutterudites and type-I clathrates. In addition, the reduction mechanism associated with an Einstein-like phonon mode was denied [1]. We have carried out $^{151}$Eu nuclear resonant inelastic scattering, a useful tool to investigate the Eu atomic dynamics in the Eu materials. The obtained spectra are completely different from those at the rare-earth sites in hexaborides and filled skutterudites by nuclear resonant inelastic scattering [9-15].

2. Experimental Results and Discussion

2.1. $^{151}$Eu Mössbauer spectroscopy

$^{151}$Eu Mössbauer measurements in the conventional way were carried out at Wako branch of RIKEN in Japan. The source used is 100 mCi of $^{151}$SmF$_3$. The Doppler velocity was calibrated by $^{57}$Fe Mössbauer spectroscopy of $\alpha$-Fe at 295 K. The measured sample was crushed into powder from polycrystalline ingot of Eu$_3$Pd$_{20}$Ge$_6$.

The $^{151}$Eu Mössbauer spectrum of Eu$_3$Pd$_{20}$Ge$_6$ at 295 K is shown in Fig. 1. The spectrum consists of three components in spite of two Eu crystallographic sites in this compound. The isomer shift of one component around 0 mm/sec corresponds to a trivalent state, that of a second component around -10 mm/sec to a divalent state and that of the third component to an intermediate valence state. Since the previous magnetic susceptibility measurement suggests that Eu$_3$Pd$_{20}$Ge$_6$ is a valence fluctuating compound, Eu valence fluctuations are possibly observed in both crystallographic sites. Under this assumption, the spectrum of the one site consists of that with the intermediate valence state and the
spectrum of the other site consists of that with both the divalent and trivalent states. In this case, the spectral weight of the one to the other is $1 : 2$, consistent with the volume fraction of Eu sites expected from the crystallographic point of view. Therefore, the former component shows the spectrum at the 4a site and the latter one shows that at the 8c site. In addition, since the spectral weight of these components shows no temperature dependence [16], this spectral assignment is not inconsistent with the number of the crystallographic sites.

Significant difference of the valence state is observed between $^{151}$Eu Mössbauer spectroscopy and Eu L$_3$-edge X-ray absorption spectroscopy. No components of the intermediate valence state, which corresponds to the component of the 4a site, are observed in the X-ray absorption spectroscopy [16]. Since the time window of the X-ray absorption spectroscopy is shorter than that of the $^{151}$Eu Mössbauer spectroscopy, this is direct evidence that the Eu valence at least at the 4a site of Eu$_3$Pd$_{20}$Ge$_6$ is fluctuating with a frequency matching the time window of the $^{151}$Eu Mössbauer spectroscopy, hence several hundreds MHz.

2.2. $^{151}$Eu Nuclear Resonant Inelastic Scattering

$^{151}$Eu nuclear resonant inelastic scattering experiments were carried out at BL09XU of SPring-8 in Japan. The high resolution monochromator is the nested-type one which consists of Si(4 2 2) and Si(12 8 8) reflections. The resolution of this optics is 1.5 meV at the $^{151}$Eu Mössbauer resonance of 21.5 keV. The 203 bunches operation of SPring-8, whose interval is 23.6 nsec, is chosen for this experiment. The used detector is a multi-element avalanche photo-diode detector.

The nuclear resonant inelastic scattering spectrum of Eu$_3$Pd$_{20}$Ge$_6$ at 300 K is shown in Fig. 2. This differs from the spectra of other cage-structured compounds [9-15]. In the previous works of the single-site cage-structured compounds, the spectra at the inserted atomic sites (guest sites) consist of a sharp excitation, indicating the presence of Einstein-like modes. However, the spectra obtained in the present work contain much larger contribution to the acoustic modes than the other cage-structured compounds. Although it has been believed that the Einstein-like modes reduce the thermal conductivity in most of cage structured compounds, the present result agrees with the proposed reduction mechanism without any Einstein-like modes in Ref. 1.

Concerning the correlation of the Eu valence fluctuation and atomic motion, a significant temperature dependence of the average force constant is found in the present work. The average force constants obtained by the Lipkin’s sum rule [17] are 115.7 and 100.7 N/m at 300 and 6 K, respectively. Since the Eu valence state obtained by both $^{151}$Eu Mössbauer spectroscopy and Eu L$_3$-edge XAS are

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Figure 2. $^{151}$Eu nuclear resonant inelastic scattering spectra of Eu$_3$Pd$_{20}$Ge$_6$ at 6 and 300 K.
different between 300 and 6 K, the reduction of the force constant may correlates with the change of the Eu valence [16].

3. Summary
Eu charge and atomic dynamics in Eu$_3$Pd$_{20}$Ge$_6$ were investigated by $^{151}$Eu Mössbauer spectroscopy and $^{151}$Eu NRIS. The obtained $^{151}$Eu Mössbauer spectrum at 295 K demonstrates that valence fluctuations with different frequency are realized in this compound. The $^{151}$Eu nuclear resonant inelastic scattering spectrum differs from the spectra at the guest sites in other cage-structured compounds.

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