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The Eu valence state and valence transition in $\text{Eu}(\text{Pd}_{1-x}\text{Pt}_x)_2\text{Si}_2$

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Abstract. We examine the temperature dependence of the Eu valence and lattice parameters for $\text{Eu}(\text{Pd}_{1-x}\text{Pt}_x)_2\text{Si}_2$ by means of x-ray absorption spectroscopy (XAS) and x-ray diffraction, respectively. Strong temperature dependence of the Eu valence was observed for $\text{Eu}(\text{Pd}_{1-x}\text{Pt}_x)_2\text{Si}_2$. Combining the Mössbauer effect data and XAS results, we estimated the Eu valence as a function of temperature. It is shown that the Eu valence in the ground state shows very little sensitivity to x for $0 \leq x \leq 0.10$. In the temperature dependence of the Eu valence, the compound with $x = 0.05$ undergoes a continuous valence change, while the one with $x = 0.15$ shows a first-order valence transition. The factors determining the Eu valence in $\text{Eu}(\text{Pd}_{1-x}\text{Pt}_x)_2\text{Si}_2$ are discussed.

1. Introduction

For the last two decades, it has been manifested that 4f or 5f electrons are often destabilized or delocalized in compounds and alloys. Such a feature causes various kinds of exotic phenomena, such as valence fluctuation, the dense Kondo effect, and Kondo semiconductor and heavy-fermion behaviour. Much active research has already been carried out with the aim of achieving an understanding of the mechanisms of these phenomena.

In particular, some Eu-based compounds are known to exhibit quite a large valence change versus temperature [1–5]. In general, a Eu ion is either in a divalent state ($4f^7$) or in a trivalent one ($4f^6$). The former is characterized by a half-filled shell providing pure spin magnetism ($S = J = 7/2$, $L = 0$). On the other hand, the latter is the nonmagnetic ground state ($S = L = 3$, $J = 0$). The valence change occurs between these two states. For instance, EuPd_2Si_2 , which crystallizes in the tetragonal ThCr_2Si_2 -type structure, undergoes a precipitous yet continuous Eu valence change from 2.8 to 2.2 in the temperature range of 130–170 K with increasing temperature [2, 3].

Noting a large difference in the magnetic moment between the divalent ($7 \mu_B$) and trivalent (0) states, we have investigated magnetic field effects on Eu valence and found that EuPd_2Si_2 exhibits a valence transition under a high magnetic field [6, 7]. This transition, which occurs at around 93 T at 6 K, is accompanied with a large hysteresis, demonstrating that the transition is of first order. This behaviour is in contrast to a continuous transition induced by temperature. In order to investigate this transition further, we substituted Pt for Pd in EuPd_2Si_2 [6, 7]. With increasing Pt content x , both the transition field (H_v) and the transition temperature (T_v) are lowered. In addition, the field-induced transition remains sharp with a large hysteresis.

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These results suggest that the substitution of Pt for Pd only shifts the energy scale of the valence transition and that the so-called alloying effects are negligible in the present system. On the other hand, the temperature-induced valence transition of $\text{Eu}(\text{Pd}_{1-x}\text{Pt}_x)_2\text{Si}_2$ has not been investigated in detail. The valence transition temperature was estimated only from the susceptibility measurements [7].

In this paper, we will report the nature of the temperature-induced valence transition of $\text{Eu}(\text{Pd}_{1-x}\text{Pt}_x)_2\text{Si}_2$. We performed L_{III} x-ray absorption spectroscopy (XAS) and x-ray diffraction (XRD) measurements at various temperatures. The former gives direct observations of the Eu valence changes. The L_{III} -edge spectrum of a rare-earth system is characterized by an intense ‘white line’ caused by excitation of a 2p core electron into an empty 5d state above the Fermi level. In valence-fluctuating systems, two white-line peaks separated by 7–8 eV, corresponding to the two valence states, are observed, since the probe time ($\sim 10^{-15}$ s) is much shorter than the valence-fluctuation time [8, 9]. On the other hand, the latter gives more macroscopic information on the valence transition. A thermal expansion anomaly accompanied by the valence transition is observed due to the ionic size of Eu^{2+} being a few per cent larger than that of Eu^{3+} . In addition, it gives information about whether the valence transition is continuous or of first order, since Bragg lines in XRD are reflected by macroscopic regions of the sample [2, 10, 11]. The lattice parameters a and c are estimated from a few Bragg peaks in order to check the anisotropic behaviour of the thermal expansion anomaly. On the basis of the results, the nature of the valence transition of $\text{Eu}(\text{Pd}_{1-x}\text{Pt}_x)_2\text{Si}_2$ and the effects of Pt substitution on the Eu valence are discussed in comparison with the previous results for $\text{Eu}(\text{Pd}_{1-y}\text{Au}_y)_2\text{Si}_2$.

2. Experimental procedure

$\text{Eu}(\text{Pd}_{1-x}\text{Pt}_x)_2\text{Si}_2$ ($x = 0.05, 0.10$ and 0.15) ingots were prepared by arc melting under a purified argon atmosphere. Firstly, $\text{Pd}_{1-x}\text{Pt}_x\text{Si}$ alloys were prepared. Secondly, the mixture of Eu and $\text{Pd}_{1-x}\text{Pt}_x\text{Si}$ was melted several times. In this procedure, an excess of 5 at.% Eu was added to compensate for the loss of Eu during melting. The ingots, wrapped in tantalum foil, were then annealed in an evacuated quartz tube at 800°C for one week.

The samples were checked by means of XRD using a Rigaku diffractometer with Fe $K\alpha$ radiation. Since EuPt_2Si_2 forms the CaBe_2Ge_2 -type structure [12], where the layer stacking is a little different from that in the ThCr_2Si_2 -type structure, there certainly exists a solubility limit for $\text{Eu}(\text{Pd}_{1-x}\text{Pt}_x)_2\text{Si}_2$ with ThCr_2Si_2 -type structure. The XRD patterns at room temperature show that the samples with $x = 0.05$ and 0.10 have a single phase with the ThCr_2Si_2 -type structure. In the case of $x = 0.15$, some extra peaks with a very small intensity were observed at $2\theta = 30\text{--}40^\circ$. Analysis of these peaks reveals that the sample with $x = 0.15$ contains a small amount of an impurity phase with the CaBe_2Ge_2 structure. However, according to our previous studies [7], with increasing x up to 0.15 , both the valence transition temperature and the field decrease linearly, and the lattice constant c derived from the main peaks in the XRD increases substantially. (The lattice constant a is almost independent of x .) These results demonstrate that the Pt concentration of the main phase of the sample with $x = 0.15$ is almost 15%. The samples for this study were cut from the same ingots as were used for the magnetization measurements in references [6] and [7]. The L_{III} XAS measurements from 10 K to 290 K were performed by using photons modulated with a Si(111) monochromator at BL-7C in the Photon Factory of KEK. The temperature-dependent XRD measurements were carried out in the temperature range of 10–300 K. During both measurement procedures, each sample was cooled by a closed-cycle helium refrigerator and held at a constant temperature by a temperature controller.

3. Results

Figure 1 shows the x-ray absorption near-edge spectra at the Eu L_{III} threshold for the sample with $x = 0.10$ at three typical temperatures, above, near and below the valence transition temperature, T_v . They are apparently interpretable as superpositions of two white lines. From the intensity ratio of the two white lines, the fractional occupation of the 4f configurations can be obtained. Evidently, the Eu valence changes with temperature in the 10% Pt-substituted compound, as expected from the temperature dependence of the magnetic susceptibility [6, 7]. Similar behaviour of the L_{III} XA spectra is observed also for the compounds with $x = 0.05$ and 0.15. The spectra were fitted with two subspectra, consisting of an arctangent and a Lorentzian, for the $2p^54f^75d^*$ and $2p^54f^65d^*$ final-state components in order to estimate the Eu valence. The fits of the data are also presented in figure 1. The dashed-dotted and the dashed line indicate the subspectra for the Eu^{2+} and Eu^{3+} final-state components, respectively. These Lorentzian intensities give a ratio of two Eu valence states.

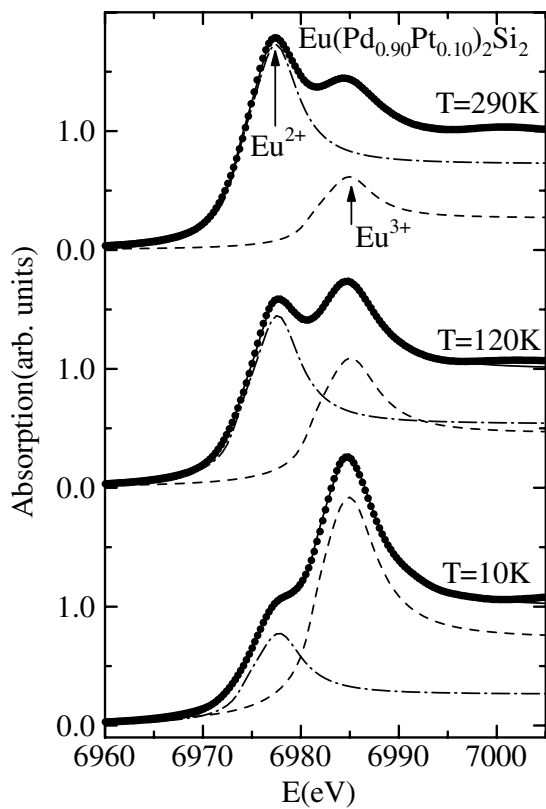


Figure 1. X-ray absorption near-edge spectra at the Eu L_{III} threshold of $\text{Eu}(\text{Pd}_{0.90}\text{Pt}_{0.10})_2\text{Si}_2$ at three typical temperatures. The dashed-dotted and the dashed line indicate the Eu^{2+} $2p^54f^75d^*$ and Eu^{3+} $2p^54f^65d^*$ final-state components, respectively.

Figure 2 shows the Eu valence of $\text{Eu}(\text{Pd}_{1-x}\text{Pt}_x)_2\text{Si}_2$ with $0.05 \leq x \leq 0.15$ estimated from L_{III} XAS measurements as a function of temperature. It is confirmed that each sample undergoes a valence change in the temperature ranges where the magnetic susceptibility begins to deviate from the Curie–Weiss law [7]. However, the Eu valence estimated from L_{III} XAS measurements is subject to some ambiguity, because the present samples contain a certain amount of Eu^{2+} as impurities. This is observed as a Curie tail in the susceptibility versus temperature curves at low temperatures shown in figure 2 in reference [7]. The presence of such impurities is also confirmed for our samples by Mössbauer spectroscopy [13]. However, in

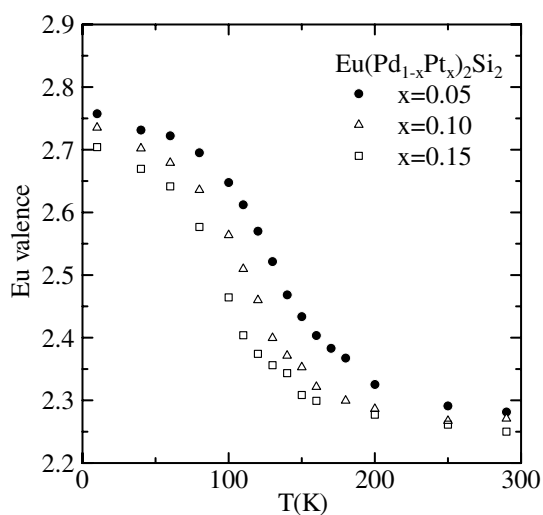


Figure 2. The temperature dependence of the Eu valence for the compounds with $x = 0.05$, 0.10 and 0.15 determined from the XA spectra.

the XRD patterns of the samples with $x = 0.05$ and 0.10, we could not detect any other phases within the experimental accuracies. In most of the studies on EuPd_2Si_2 , such Eu^{2+} impurities have been reported and considered as due to site exchanges of the Pd and Si ions [8, 9, 14–17]. This unavoidable problem always causes an error bar for the Eu valence. Detailed discussion of and corrections to the Eu valence will be given in the following section.

Figure 3 shows (200) Bragg peaks at different temperatures around T_V for $x = 0.05$ and 0.15. The (200) peak was chosen because the change in the Eu valence in EuPd_2Si_2 is

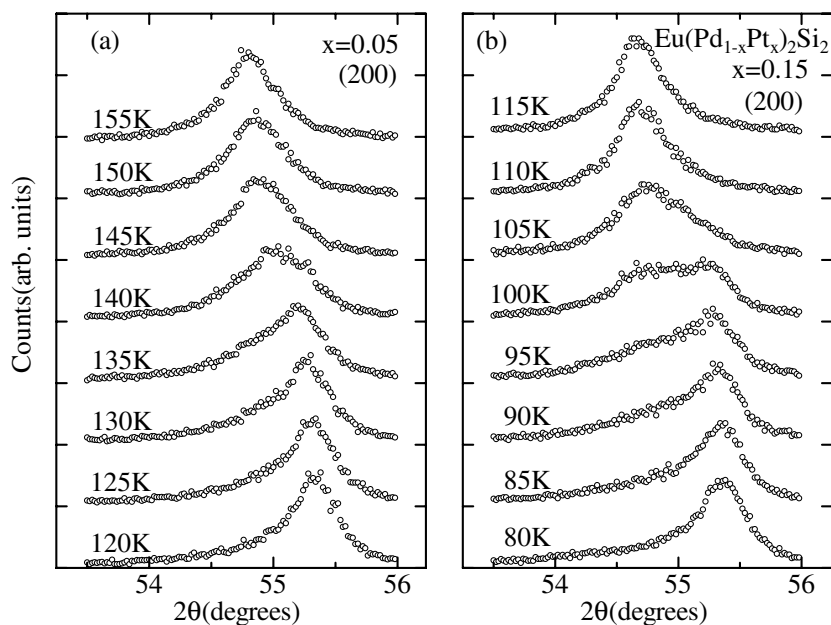


Figure 3. The (200) Bragg peaks of the compounds with $x = 0.05$ and 0.15 at around the valence transition temperature.

directly reflected in the lattice constant a . In addition, the (200) peak has enough intensity and no adjacent peaks. For $x = 0.05$, a single peak shifts gradually toward a low angle with increasing temperature, implying that the compound with $x = 0.05$ retains a single phase, whose lattice parameter changes steeply but continuously through the valence transition. In contrast, for $x = 0.15$, two distinct (200) peaks coexist at around T_v with continuous intensity transfer from one peak to the other, indicating a first-order phase transition. The compound with $x = 0.10$ is on the verge of showing a first-order phase transition, suggesting that the critical point separating a continuous valence change from a first-order valence transition is near $x = 0.10$. These results are in good agreement with the Mössbauer effect measurements [13].

Figure 4 shows the temperature dependence of the lattice parameters, a and c , and the unit-cell volume, V , estimated from the XRD measurements. Anomalous increases in a and V are seen at around T_v . The relative volume change $\Delta V/V$, associated with the valence transition,

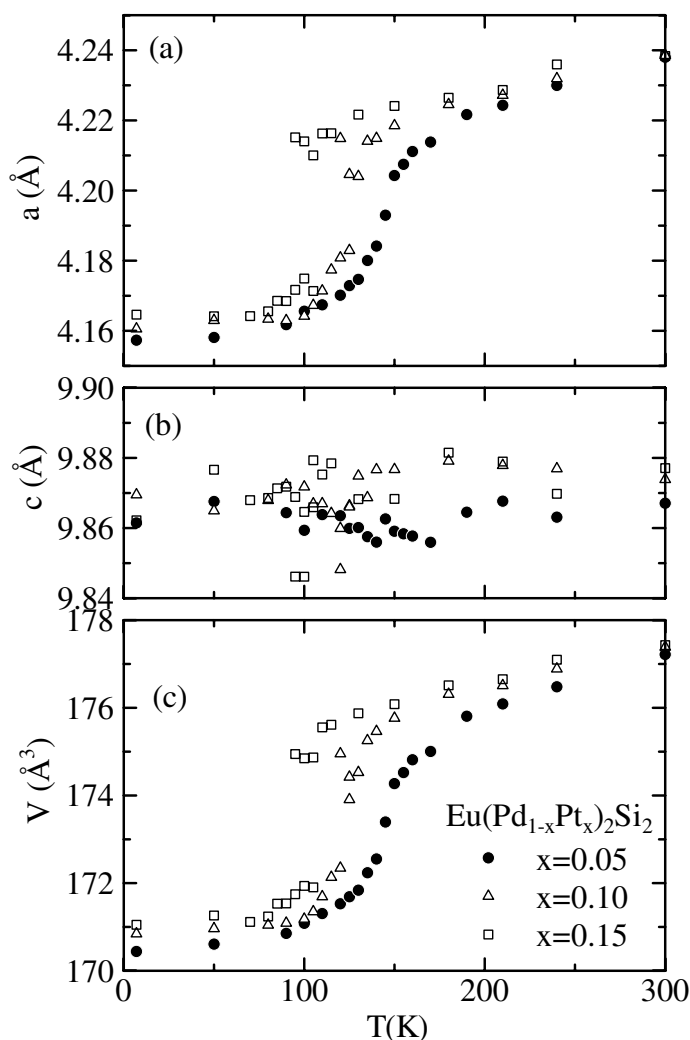


Figure 4. Temperature dependences of the lattice parameters, a (a) and c (b), and the unit-cell volume V (c).

is about 2%, which is comparable with the difference in ionic size between Eu^{2+} and Eu^{3+} . At around T_v , two phases coexist in a narrow temperature region, which suggests that the sample is relatively homogeneous and that the alloying effect is small. Unlike the lattice parameter a , which shows a large variation, c seems to be, on the whole, independent of temperature. Such anisotropic behaviour, which is also observed in EuPd_2Si_2 [2] and $\text{Eu}(\text{Pd}_{0.9}\text{Au}_{0.1})_2\text{Si}_2$ [18], was explained by Sampathkumaran *et al* [2] as follows: in RT_2X_2 (R: rare earth; T: transition metal; X: Si, Ge, P), which crystallizes in the tetragonal ThCr_2Si_2 -type structure, a depends on the R radius, whereas c is determined by the T–X skeleton. The temperature dependence of the lattice parameters of $\text{Eu}(\text{Pd}_{1-x}\text{Pt}_x)_2\text{Si}_2$ seems to be in good agreement with this explanation. The valence transition temperature, T_v , estimated from XRD measurements is shown in figure 5 as a function of Pt content. With increasing x , T_v decreases nearly linearly.

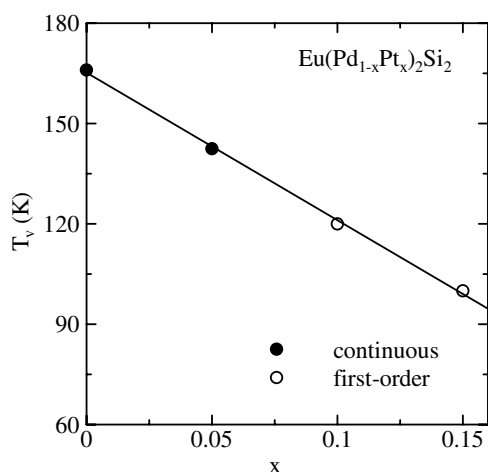


Figure 5. The dependence on the Pt content x of the valence transition temperature T_v estimated from XRD measurements.

4. Discussion

First, we discuss the Eu valence in $\text{Eu}(\text{Pd}_{1-x}\text{Pt}_x)_2\text{Si}_2$. As mentioned in the previous section, the Eu valence estimated from L_{III} XAS measurements is subject to some ambiguity. In L_{III} XAS measurements, the Eu^{2+} and Eu^{3+} components of the intermediate-valence state are observed independently. If the sample contains a small amount of Eu^{2+} -state impurity, the Eu^{2+} component is overestimated, which leads to underestimation of the Eu valence of the main phase. Another important method for estimating Eu valence is ^{151}Eu Mössbauer spectroscopy. It is generally accepted that the isomer shift (IS) has a linear relation with the Eu valence, v . Recently, Görlich performed Mössbauer effect measurements on $\text{Eu}(\text{Pd}_{1-x}\text{Pt}_x)_2\text{Si}_2$ using samples obtained from the same ingots as for the present measurements [13]. According to their results, the IS at 4.2 K for $\text{Eu}(\text{Pd}_{1-x}\text{Pt}_x)_2\text{Si}_2$ relative to SmF_3 is in the range of -0.75 mm s^{-1} to -1.0 mm s^{-1} for x increasing from 0.05 to 0.15. These IS values are comparable to that of EuPd_2Si_2 at 4.2 K, $-0.53 \pm 0.05 \text{ mm s}^{-1}$, reported by Schmiester *et al* [14]. Roughly speaking, a ΔIS of 10 mm s^{-1} corresponds to a Δv of at most 1 [8,9]. Therefore, the Mössbauer results suggest that substituting 15% Pt for Pd causes a slight change of the Eu valence in the ground state, at most $\Delta v = 0.05$. Keeping this in mind, we will correct the Eu valence estimated from L_{III} XAS. The Mössbauer measurements have also shown that the absorption spectra of $\text{Eu}(\text{Pd}_{1-x}\text{Pt}_x)_2\text{Si}_2$ at 4.2 K consist of a main line at around $\text{IS} = -1 \text{ mm s}^{-1}$ and a weak satellite line at the Eu^{2+} position. Such a satellite line has been reported in all

Mössbauer studies of EuPd_2Si_2 with varying intensities [8, 9, 14–17]. The analyses of the spectra have revealed that the relative intensity of the satellite line is 9%, 10% and 25% for $x = 0.05, 0.10$ and 0.15 , respectively [13]. Assuming that a satellite line originates from the Eu^{2+} -state impurities independently of temperature, we can calculate the corrected Eu valence from $(v_{\text{XAS}} - 2)/(1 - p_{\text{imp}}) + 2$, where v_{XAS} and p_{imp} denote the Eu valence estimated from XAS (shown in figure 2) and the amounts of the impurities derived from Mössbauer effect measurements at 4.2 K, respectively. The relative intensity of the satellite line was almost independent of temperature between 4.2 K and 10 K. Figure 6 displays the corrected valence for $x = 0.05$ and 0.10 as a function of temperature. The results suggest that the Eu valence at low temperatures shows very little sensitivity to x , being 2.83 for $0.05 \leq x \leq 0.10$. For $x = 0.15$, however, we have $v = 2.94$ at 10 K, which is considerably larger than that for $x \leq 0.10$. Presumably, this is because the amount of impurity estimated from Mössbauer studies is too large for $x = 0.15$. As described above and in reference [7], $x = 0.15$ is close to the critical concentration at which $\text{Eu}(\text{Pd}_{1-x}\text{Pt}_x)_2\text{Si}_2$ begins to show the ThCr_2Si_2 structure. A small amount of impurity phase with the CaBe_2Ge_2 structure was observed in the XRD pattern for $x = 0.15$. This is also supported by the fact that for $x = 0.05$ and 0.10 at 4.2 K, the satellite line of the Mössbauer spectrum exhibits a single peak, while for $x = 0.15$, it shows a hyperfine splitting [13], which could be ascribed to the impurity phase with the CaBe_2Ge_2 structure since EuPt_2Si_2 orders antiferromagnetically at 15 K [12]. We believe that the existence of the impurity phase with the CaBe_2Ge_2 structure makes it difficult to correct the Eu valence estimated from the XAS for $x = 0.15$.

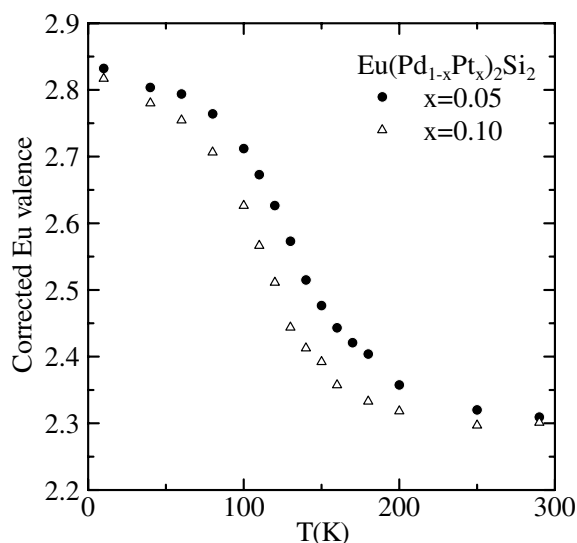


Figure 6. The temperature dependence of the Eu valence corrected using the Mössbauer results [13] for $x = 0.05$ and 0.10 .

Combining the data from the L_{III} XAS and Mössbauer effect, we have shown that the Eu valence in the ground state has very little sensitivity to the Pt content in $\text{Eu}(\text{Pd}_{1-x}\text{Pt}_x)_2\text{Si}_2$ for $x \leq 0.15$. This is in contrast to the case for $\text{Eu}(\text{Pd}_{1-y}\text{Au}_y)_2\text{Si}_2$, for which Δv estimated from the IS is more than 0.1 with y increasing from 0 to 0.15 [19]. Thus, the Pt substitution for EuPd_2Si_2 has a gentle effect on the Eu valence compared with Au substitution. We point out that the Eu valence in $\text{Eu}(\text{Pd}_{1-x}\text{Pt}_x)_2\text{Si}_2$ and $\text{Eu}(\text{Pd}_{1-y}\text{Au}_y)_2\text{Si}_2$ may be related to the lattice parameter a or the unit-cell volume V in these systems. Figure 7 displays the concentration dependence of the lattice parameters a and c and the volume V of $\text{Eu}(\text{Pd}_{1-x}\text{Pt}_x)_2\text{Si}_2$ at room temperature together with the data for $\text{Eu}(\text{Pd}_{1-y}\text{Au}_y)_2\text{Si}_2$ reported by Sauer *et al* [18]. The

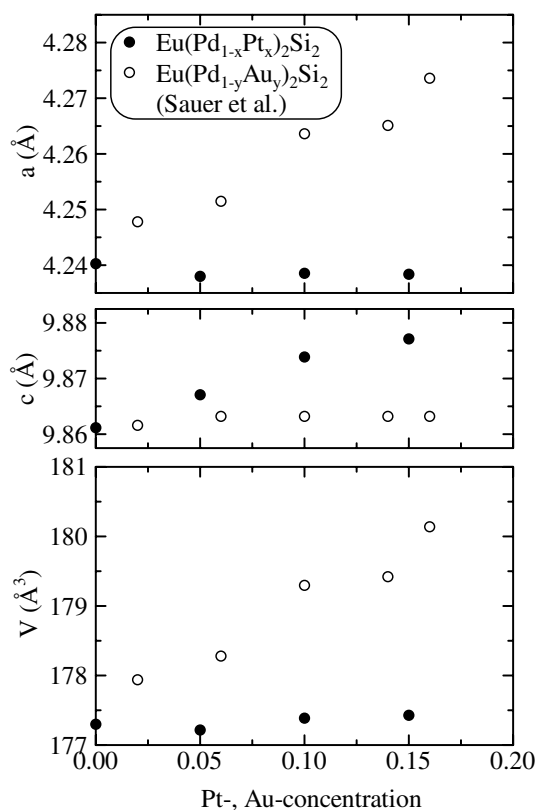


Figure 7. Pt and Au concentration dependences of the lattice parameters a and c , and the unit-cell volume V of $\text{Eu}(\text{Pd}_{1-x}\text{Pt}_x)_2\text{Si}_2$ and $\text{Eu}(\text{Pd}_{1-y}\text{Au}_y)_2\text{Si}_2$ [18] at room temperature. These systems exhibit opposite trends.

lattice parameter a and the volume V depend weakly on x , and c increases nearly linearly with x in $\text{Eu}(\text{Pd}_{1-x}\text{Pt}_x)_2\text{Si}_2$, while the opposite trend is observed for $\text{Eu}(\text{Pd}_{1-y}\text{Au}_y)_2\text{Si}_2$. These results suggest a correlation between the Eu valence and a and/or V . This is also consistent with the fact that the valence change is reflected in the temperature dependence of a and V in $\text{Eu}(\text{Pd}_{1-x}\text{Pt}_x)_2\text{Si}_2$, as shown in figure 4. In figures 8(a) and 8(b), we plot v versus a and v versus V , respectively. In both plots, the data for $x = 0.05$ and 0.10 lie on a universal curve. Although a linear relation is found in neither plot, these plots strongly suggest that a and/or V are important factors in determining the Eu valence in $\text{Eu}(\text{Pd}_{1-x}\text{Pt}_x)_2\text{Si}_2$. One may claim that the electron concentration is an alternative factor influencing the Eu valence. Of course, the electron concentration is expected to have a certain effect on the Eu valence. However, the substitution of Ge for Si in EuPd_2Si_2 expands both a and c significantly and causes a considerable valence change of Eu, although the electron concentration is kept constant [20]. Therefore the lattice parameter or volume has more impact on the Eu valence.

For $x \leq 0.05$, the Eu valence changes continuously with temperature, while the compound with $x = 0.15$ undergoes a first-order phase transition. The critical concentration is near $x = 0.10$. Such a nature of the valence transition is also observed for $\text{Eu}(\text{Pd}_{1-y}\text{Au}_y)_2\text{Si}_2$ [11]. So far, we have discussed the valence transition in the framework of the interconfigurational fluctuation (ICF) model [21, 22]. The detailed explanation of this model is described in references [7] and [23]. Briefly, assuming a trivalent state as the ground state, a thermal

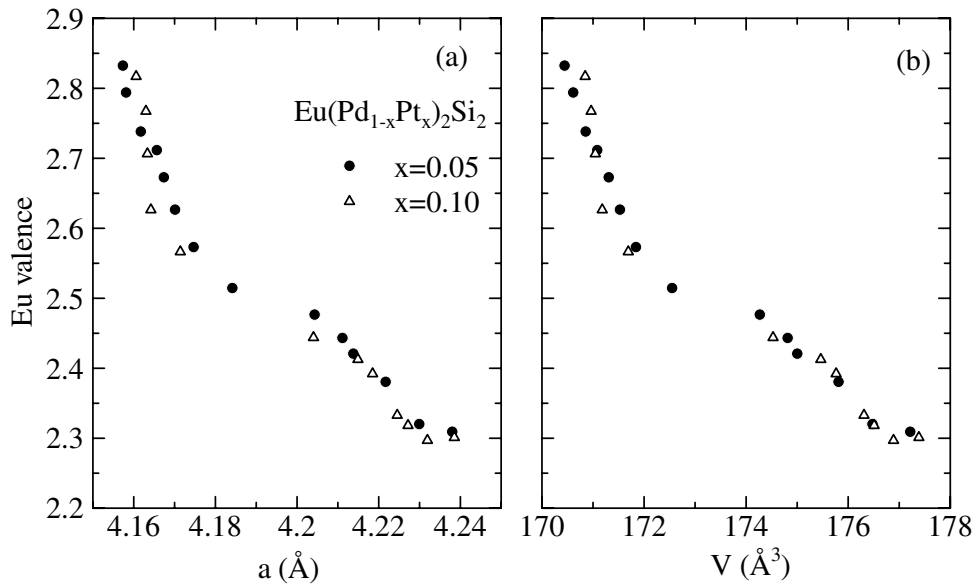


Figure 8. (a) A plot of the corrected Eu valence versus the lattice parameter a . (b) A plot of the corrected Eu valence versus the unit-cell volume V . In both plots, the data for $x = 0.05$ and 0.10 lie on a universal curve.

excitation to a divalent state, which is located at higher energy E_{ex} than the ground state, induces the valence change. Furthermore, to describe the cooperative phenomenon of the valence transition, it has been assumed that the excitation energy E_{ex} depends on the probability of there being a divalent state, p_2 , as $E_{\text{ex}} = E_0(1 - \alpha p_2)$, where E_0 and α are parameters [21]. In a previous paper, we have shown that the valence transition changes from a continuous one to a first-order-type one as E_0 is decreased [23]. Lowering T_v with decreasing E_0 is a natural consequence. We note that the excited state (Eu^{2+}) has a larger size than the ground state (Eu^{3+}); the substitution of larger atoms decreases the energy separation, E_0 , which makes the transition sharper. The nature of the valence transition in $\text{Eu}(\text{Pd}_{1-x}\text{Pt}_x)_2\text{Si}_2$ is also understood in this scenario. A similar conclusion was also given by Ghatak who used the pseudospin model [24].

5. Conclusions

We have performed L_{III} XAS and XRD measurements on $\text{Eu}(\text{Pd}_{1-x}\text{Pt}_x)_2\text{Si}_2$ with $0.05 \leq x \leq 0.15$. It was directly evidenced that $\text{Eu}(\text{Pd}_{1-x}\text{Pt}_x)_2\text{Si}_2$ undergoes a valence transition induced by temperature. Taking Mössbauer data into consideration, we corrected the temperature dependence of the Eu valence estimated from XAS. It was shown that the change in the Eu valence in the ground state is very small in $\text{Eu}(\text{Pd}_{1-x}\text{Pt}_x)_2\text{Si}_2$, which is in contrast to the case for $\text{Eu}(\text{Pd}_{1-y}\text{Au}_y)_2\text{Si}_2$. The XRD measurements have shown that the nature of the valence transition transforms from continuous behaviour to first-order behaviour with increasing x . In addition, the lattice parameter a and the unit-cell volume V are found to show anomalies associated with the valence change in their temperature dependences. These results strongly suggest that a and/or V are key parameters in determining the Eu valence in $\text{Eu}(\text{Pd}_{1-x}\text{Pt}_x)_2\text{Si}_2$. We conclude that substitution of Pt for Pd causes a slight change of the Eu valence state in the ground state and only lowers the valence transition temperature, T_v .

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