Effect of Rh and Ru Substitution on the Intermediate Valence of $EuPd_2Si_2$

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Introduction

The intermediate valence state of Eu is realized between Eu^{2+} ($4f^7$) and Eu^{3+} ($4f^6$) configurations. Ternary compound $EuPd_2Si_2$ is known to show strong temperature dependence of Eu valence. It undergoes a sharp but continuous valence change at around 160 K. The alloying effects on the valence change have been studied for $Eu(Pd_{1-x}Au_x)_2Si_2$ [1] and $Eu(Pd_{1-x}Pt_x)_2Si_2$ [2]. In these systems, the Eu^{2+} state becomes stable and the valence transition temperature is lowered. In order to get information on the valence behavior, we studied Eu valence of of $Eu(Pd_{1-x}Rh_x)_2Si_2$ and $Eu(Pd_{1-x}Ru_x)_2Si_2$, in which Pd is substituted by the elements with less 4*d* electron number.

Experiments

The samples were prepared in argon- arc furnace, followed by annealing 900 ^{o}C in evacuated quartz tubes for one week. The X-ray diffraction patterns show that the compounds were of single phase with the $ThCr_2Si_2$-type structure. The XAFS measurements at the Eu L_{III} edge were carreid out at BL-9A beamline of KEK Phton Factory using a Si (111) monochrometor . The samples were set in the cryocooler, of which temperature was controlled to the desired temperature of 12-290 K with an accuracy of ±0.1 K.

Results and discussion

Concentration dependences of lattice parameters a and c and the unit cell volume of $Eu(Pd_{1-x}Rh_x)_2Si_2$ and $Eu(Pd_{1-x}Ru_x)_2Si_2$ were examined. In both systems, the alloying effects on the lattice parameters are quite anisotropic: the lattice parameter, *a*, is decreased with increasing *x*, while the lattice parameter, *c*, is increased. As a result, the unit cell volume shrinks with increasing the content of guest element for both systems. The lattice parameters of 10% Ru substituted compound are nearly same as those of $Eu(Pd_{0.93}Rh_{0.07})_2Si_2$.

The temperature dependence of the Eu valence estimated from L_{III} edge spectra is shown in Fig. 1. It is found that the valence transition temperature shifts towards low temperatures with increasing Rh content from zero to 15%, whereas no significant change has been observed for 10% Ru substituted compound. These results indicate that Rh substitution makes the Eu^{2+} state stable.

It has been recognized that the stability of Eu^{2+} state is related to lattice expansion, because the atomic volume of Eu^{2+} ion is 2-3% larger than that of Eu^{3+} ions. Previous work on Au and Pt substituted compounds support this scenario. However, our results suggest that the lattice expansion is not the origin of the stability the Eu^{2+} state, because the unit cell volume is decreased in $Eu(Pd_{1-x}Rh_x)_2Si_2$. One may claim that the lattice parameter *c* is responsible for stabilizing the divalent state. This is ruled out, because the valence change is not reflected in the temperature dependence of lattice parameter *c* in $EuPd_2Si_2$. The Ru substitution has no influences on the valence transition of $EuPd_2Si_2$, although the lattice parameters and the unit cell volume show similar concentration dependence to the Rh substituted system. We believe that the electronic concentration is an alternative factor for determining the valence state in the Eu systems. Presumably, the decrease of electron concentration stabilizes the Eu^{2+} state, which overcomes the lattice shrinkage effect in these two systems.

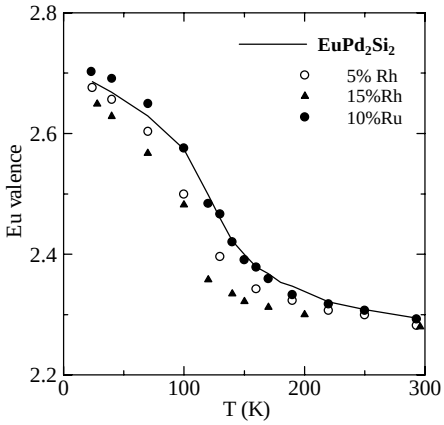

Fig.1 Temperature dependence of the Eu valence of $Eu(Pd_{1-x}Rh_x)_2Si_2$ and $Eu(Pd_{1-x}Ru_x)_2Si_2$ estimated from the Eu L_{III} XAFS measurements.

References

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