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Field-induced valence transition of $Eu(Pd_{1-x}Pt_x)_2Si_2$

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The magnetic susceptibility and high-field magnetization have been measured for the intermediate valence system $Eu(Pd_{1-x}Pt_x)_2Si_2$ with $0 \leqslant x \leqslant 0.15$. A first-order valence transition is observed for all the compounds under high field of 100 T at low temperatures. This valence transition is of first order accompanied with a large hysteresis, which is in contrast to a continuous valence change against temperature. Based on the interconfigurational fluctuation (ICF) model, the temperature- and field-induced valence transitions are discussed. It is found that a first-order valence transition can be induced by magnetic field, even if the system shows a continuous valence transition against temperature. Metamagnetic behavior at finite temperatures is also understood qualitatively by the ICF model. [S0163-1829(97)06817-3]

I. INTRODUCTION

Some Eu-based compounds are known to show intermediate valence between Eu^{3+} ($4f^6$) and Eu^{2+} ($4f^7$) configurations. Among them, $EuPd_2Si_2$ with the tetragonal $ThCr_2Si_2$-type structure has attracted considerable attention due to its characteristic temperature-induced valence change. This compound undergoes a precipitous, yet continuous, valence change at around 170 K.[1] According to the Mössbauer effect[1] and L_{III} x-ray absorption spectroscopy[2,3] (L_{III}-XAS) the Eu valence is nearly 2.8 below 130 K, while it suddenly changes to 2.3 above 180 K. These measurements have established that $EuPd_2Si_2$ is on the verge of a first-order valence transition.

In order to investigate the nature of this valence transition, various kinds of experiments, such as substitution effects and pressure effects, have been extensively investigated. Especially, the substitution of Au for Pd leads to interesting results.[4,5] With increasing Au content in the system $Eu(Pd_{1-y}Au_y)_2Si_2$, the valence transition is depressed in temperature and it becomes a first-order phase transition at $0.05 \leqslant y \leqslant 0.18$. Moreover, an antiferromagnetic order appears at $y > 0.18$, where a divalent state is stabilized in the whole temperature range. The valence transition of $EuPd_2Si_2$ is also sensitive to pressure. Schmiester *et al.* have found that applying pressure makes the valence transition more gradual and increases the valence transition temperature.[6]

In contrast to these experiments, less attention has been paid to the magnetic field effects on the intermediate valence of $EuPd_2Si_2$ so far. In the early stage, the high-field magnetization measurements were employed to estimate the intrinsic susceptibility of $Eu(Pd_{1-y}Au_y)_2Si_2$,[4] but no significant effects of the magnetic field on the valence transition have been studied. However, considering a large difference of J between the Eu^{2+} ($J=7/2$) and Eu^{3+} ($J=0$) configurations, the Eu valence must be affected by high magnetic fields.

Recent developments in high-field generation have enabled us to measure magnetizations up to 100 T. Quite recently, we have measured the high-field magnetization of $EuPd_2Si_2$ and have observed a metamagnetic transition at $H=93$ T.[8] This is the first example of a field-induced valence transition of the Eu-based compounds. In order to study the relation between the field- and temperature-induced valence transitions, further experiments have been desired.

This paper presents the magnetic properties of $Eu(Pd_{1-x}Pt_x)_2Si_2$ including the high-field magnetization up to 100 T. Here, the $Eu(Pd_{1-x}Pt_x)_2Si_2$ system was studied instead of $Eu(Pd_{1-y}Au_y)_2Si_2$, because Pd and Pt belong to the same group in the Periodic Table and the substitution effects on the Pt-substituted system are expected to be milder than those on the Au-substituted system. In Sec. II, we describe the experimental details, especially the sample preparation procedure. The experimental results are presented in Sec. III. Based on the experimental results, the origin of the temperature- and field-induced valence transitions will be discussed in terms of the interconfigurational fluctuation (ICF) model in Sec. IV. Conclusions are given in Sec. V.

II. EXPERIMENTS

The $Eu(Pd_{1-x}Pt_x)_2Si_2$ ($x=0$, 0.05, 0.10, 0.15, and 0.20) samples were prepared by arc-melting constituent elements with the purities better than 99.9% under purified argon atmosphere. The melting points of Pd (1555 °C) and Si (1414 °C) are much higher than that of Eu (822 °C), even being comparable to its boiling point (1597 °C). On the other hand, the binary compound PdSi has a melting point of 908 °C.[7] Therefore, we melted $Pd_{1-x}Pt_xSi$ alloys prior to preparing ternary or quaternary compounds. Subsequently, the mixture of Eu and $Pd_{1-x}Pt_xSi$ were melted for several times. In this procedure, an excess of 5 at. % Eu was added to compensate for the loss of Eu during melting. The ingots were then annealed in an evacuated quartz tube at 800 °C for 1 week.

The samples were checked by x-ray diffraction. Since $EuPt_2Si_2$ forms the $CaBe_2Ge_2$-type structure,[9] in which the layer stacking is a little different from the $ThCr_2Si_2$ type,

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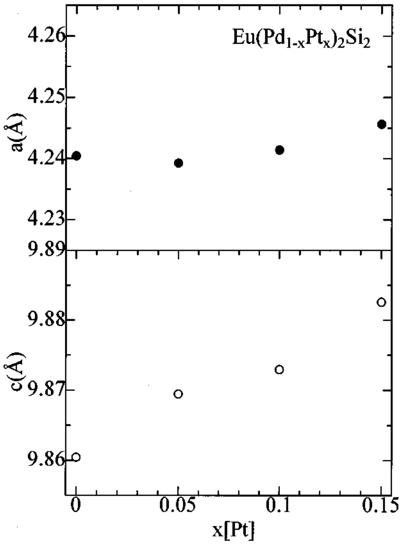

FIG. 1. Lattice parameters a and c of Eu(Pd$_{1-x}$Pt$_x$)$_2$Si$_2$ with $0\leq x\leq 0.15$ as functions of x.

there certainly exists a solibility limit in Eu(Pd$_{1-x}$Pt$_x$)$_2$Si$_2$ with ThCr$_2$Si$_2$-type structure. X-ray diffraction patterns have shown that the compounds with $0\leq x\leq 0.15$ are of single phase with ThCr$_2$Si$_2$-type structure, whereas the pattern for $x=0.20$ contains extra peaks due to an impurity phase, which are characteristic of a CaBe$_2$Ge$_2$-type phase. These results suggest Eu(Pd$_{1-x}$Pt$_x$)$_2$Si$_2$ forms a solid solution with holding the ThCr$_2$Si$_2$-type structure in the concentration range of $0\leq x\leq 0.15$. The concentration dependence of the lattice parameters a and c is shown in Fig. 1. The lattice parameter c increases nearly linearly with increasing x, whereas a is less sensitive to the Pt content. The magnetic susceptibility measurements were performed by means of a Faraday method at 8.28 kOe from 4.2 K to 270 K. The high-field magnetization process was measured up to 110 T using an induction method with well-balanced pickup coils. Ultrahigh magnetic fields up to 110 T were generated by means of a fast capacitor discharge into a single-turn coil with a 100 kJ capacitor bank. The powdered samples were used to exclude the eddy-current effect in pulsed fields.

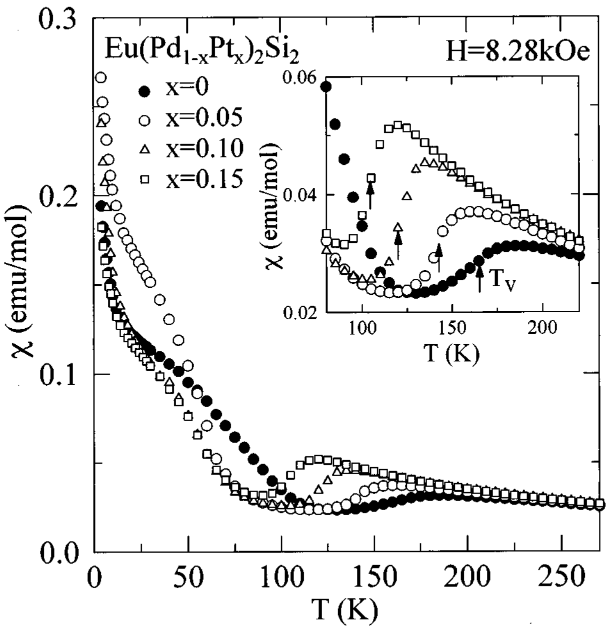

FIG. 2. Temperature dependence of the magnetic susceptibility χ of Eu(Pd$_{1-x}$Pt$_x$)$_2$Si$_2$. The inset shows χ-T curves around the valence transition temperature. Arrows indicate the valence transition temperature defined as the peak position of $d\chi/dT$.

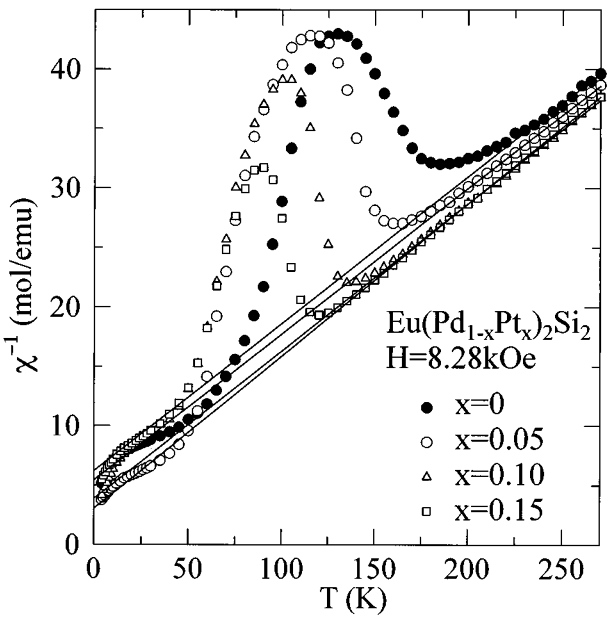

FIG. 3. Temperature dependence of the inverse susceptibility of Eu(Pd$_{1-x}$Pt$_x$)$_2$Si$_2$. The solid line shows the Curie-Weiss law.

III. RESULTS

A. Magnetic susceptibility

Figures 2 and 3 show the temperature dependence of the magnetic susceptibility and that of the inverse susceptibility of Eu(Pd$_{1-x}$Pt$_x$)$_2$Si$_2$ with $0\leq x\leq 0.15$. All the samples exhibit Curie-Weiss behavior above $T=200$ K. For $x=0$ (EuPd$_2$Si$_2$), χ deviates from the Curie-Weiss law below

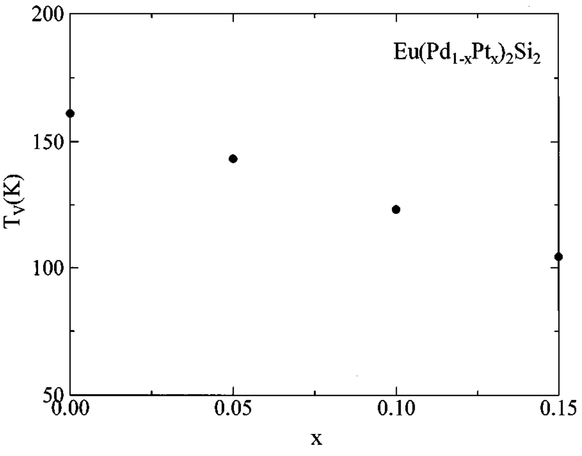

FIG. 4. Concentration dependence of the valence transition temperature T_V.

TABLE I. Data of the lattice parameters a and c, valence transition temperature T_V, effective magnetic moment μ_{eff}, Weiss temperature Θ_p, and valence transition field H_V for $\mathrm{Eu(Pd_{1-x}Pt_x)_2Si_2}$.

x	a (Å)	c (Å)	T_V (K)	μ_{eff} (μ_B/Eu)	Θ_p (K)	H_V (T)
0.00	4.239	9.865	166	8.04	−50.4	93.2
0.05	4.240	9.869	143	8.08	−44.5	79.7
0.10	4.241	9.873	120	8.03	−31.4	67.9
0.15	4.246	9.883	105	7.90	−23.5	58.3

$T = 180$ K, where the compound undergoes a continuous valence transition. For the Pt-substituted samples, χ exhibits similar behavior, but the deviation from the Curie-Weiss law starts from lower temperatures. We define the valence transition temperature T_V as the temperature where $d\chi/dT$ shows a maximum, which is indicated by arrows in the inset of Fig. 2. The concentration dependence of T_V is shown in Fig. 4, in which T_V decreases with increasing x. These results indicate that the substitution of Pt for Pd is effective to stabilize the divalent state to lower temperatures. This is reasonable, because a divalent state is stable in $\mathrm{EuPt_2Si_2}$. By the substitution of 15 at. % Pt, T_V is lowered to 105 K. This value is much higher than T_V of 50 K for the corresponding compound in the Au-substituted system.[4,5] Therefore, the effects of Pt substitution on the valence transition is milder than the Au substitution, as expected. At low temperatures below 50 K, χ again approaches to the Curie-Weiss law. This is, however, extrinsic behavior due to a ferromagnetic impurity, as pointed out by several authors.[4,10]

The effective magnetic moments μ_{eff} and the Weiss temperature Θ_p estimated from the Curie-Weiss behavior at high temperatures, are listed in Table I, together with the lattice parameters and T_V. The effective magnetic moment is in the range 7.90–8.10μ_B/Eu, being in agreement with the theoretical value for Eu^{2+}, 7.94μ_B. The Weiss temperature is negative and its absolute value decreases with increasing x.

B. High-field magnetization process

The high-field magnetization processes of the powder samples of $\mathrm{Eu(Pd_{1-x}Pt_x)_2Si_2}$ with $0 \leqslant x \leqslant 0.15$ were measured at 6 K up to 110 T. As shown in Fig. 5, a sharp and prominent jump of the magnetization ($\Delta M \sim 5\mu_B$) is observed for all the samples studied. The observed large hysteresis (~ 10 T) indicates that this metamagnetic transition is a first-order phase transition. Although the applied field reaches to the instrumental limit before the complete saturation of magnetization for $\mathrm{EuPd_2Si_2}$, the magnetization of the Pt-substituted samples is saturated at the highest field. The initial rise for all the samples in the magnetization curve is attributable to a ferromagnetic impurity, as mentioned previously. The saturation magnetization is close to $7\mu_B$/Eu, which is expected for an Eu^{2+} ion. From these results, it is concluded that the metamagnetic transition is a field-induced valence transition from an intermediate valence state to a divalent state of Eu. It should be noted that $\mathrm{EuPd_2Si_2}$ shows a continuous valence transition against temperature, while the metamagnetic transition is of first order. This point will be discussed later. The substitution of Pt for Pd lowers the metamagnetic transition field without broadening the transition. The so-called alloying effects seem to be negligible in the present system. The transition field H_V at 6 K is shown in Fig. 6 as a function of x. The mean transition field decreases nearly linearly as the Pt content increases. The hysteresis of the Pt-substituted compounds is a little wider than that of $\mathrm{EuPd_2Si_2}$.

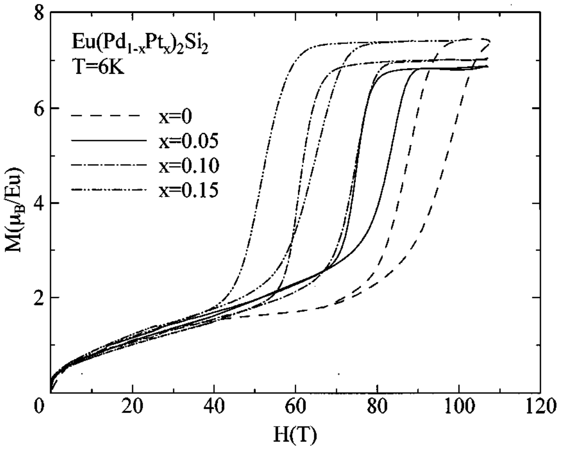

FIG. 5. High-field magnetization curves of $\mathrm{Eu(Pd_{1-x}Pt_x)_2Si_2}$ up to 110 T at $T = 6$ K.

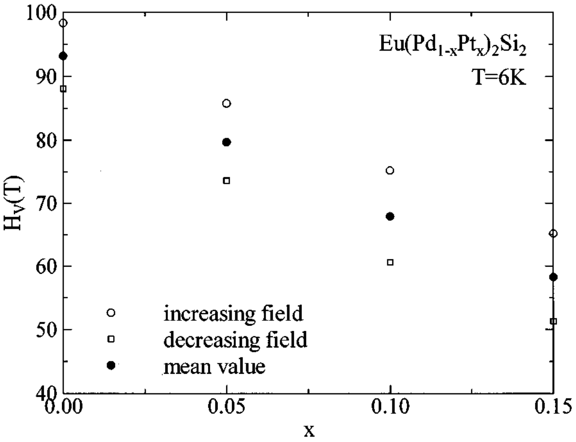

FIG. 6. Concentration dependence of the valence transition field H_V. Data in the increasing field process (open circles), decreasing field process (open squares), and the mean value (solid circles) are plotted.

Figure 7 shows the differential susceptibility as a function of magnetic field of $\mathrm{EuPd_2Si_2}$ in the decreasing field process at various temperatures. Pronounced peaks attributed to the metamagnetic transition are observed below $T = 130$ K. With increasing temperature, the peak is broadened and it shifts toward a lower field. Temperature dependence of the metamagnetic transition field is shown in Fig. 8. It is found that H_V shows a Brillouin function-type temperature dependence. The hysteresis width decreases with increasing temperature and almost vanishes at 130 K.

IV. DISCUSSION

The present results have revealed that the $\mathrm{Eu(Pd_{1-x}Pt_x)_2Si_2}$ system undergoes a valence transition under high magnetic fields. This type of valence transition

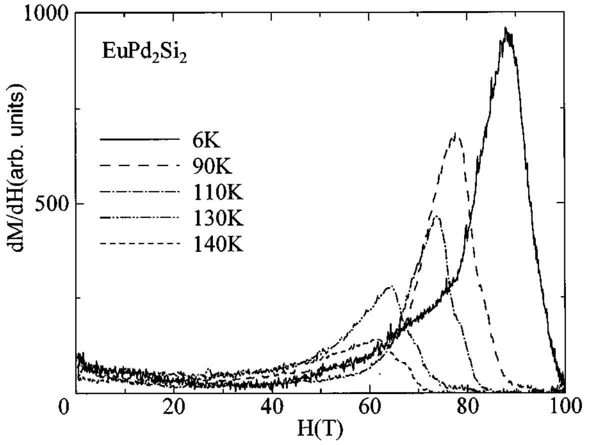

FIG. 7. Differential susceptibility as a function of magnetic field of $EuPd_2Si_2$ at various temperatures. Data in the decreasing field process are plotted.

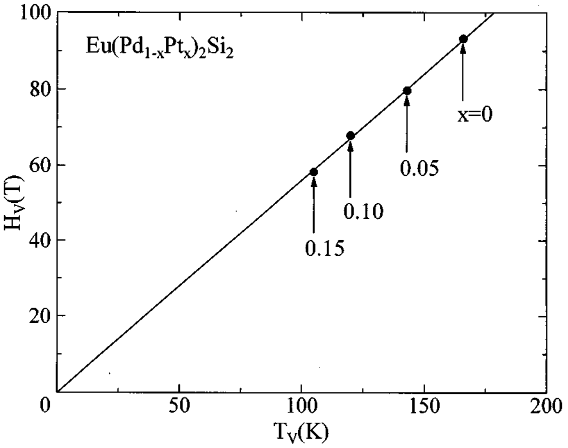

FIG. 9. H_V vs T_V plots of $Eu(Pd_{1-x}Pt_x)_2Si_2$. The solid line is to guide the eye.

was previously reported in $YbInCu_4$.[12] $YbInCu_4$ shows a first-order valence transition against temperature.[11] The Yb valence abruptly changes from 3.0 to 2.9 at $T_V = 40$ K with decreasing temperature. A clear metamagnetic transition was observed by applying magnetic field of 40 T at $T = 4.2$ K. The substitution of Ag for In increases both T_V and H_V. Katori *et al.* found that T_V is proportional to H_V in $YbIn_{1-x}Ag_xCu_4$.[13] The relation between H_V and T_V for $Eu(Pd_{1-x}Pt_x)_2Si_2$ is shown in Fig. 9. Similarly to $YbIn_{1-x}Ag_xCu_4$, a linear relation between H_V and T_V is observed in $Eu(Pd_{1-x}Pt_x)_2Si_2$. These results suggest a universal relation between H_V and T_V for the field- and temperature-induced valence transition systems.

So far, the temperature-induced valence transition of $EuPd_2Si_2$ and $YbInCu_4$ has been discussed in terms of the interconfigurational fluctuation (ICF) model.[14,15] In this model, the occupation probabilities of Eu^{2+} and Eu^{3+} configurations, denoted as p_2 and p_3, respectively, follow Boltzmann statistics,

$$\frac{p_2}{p_3} = \frac{8\exp(-E_{\mathrm{ex}}/kT^*)}{1+3\exp(-480\ \mathrm{K}/T^*)+\cdots}, \tag{1}$$

where E_{ex} is the excitation energy to convert an Eu^{3+} ion into Eu^{2+} and $T^* (= \sqrt{T^2+T_f^2})$ an effective temperature, introduced to allow a broadening of each energy level with the width of T_f. In this analysis, we use $T_f = 50$ K according to a previous literature.[16] The rapid thermal variation of Eu valence in $EuPd_2Si_2$, however, cannot be described only by this model. Croft *et al.* proposed that the excitation energy E_{ex} itself is a function of p_2,[16]

$$E_{\mathrm{ex}} = E_0(1-\alpha p_2), \tag{2}$$

where E_0 and α are constants. When p_2 increases, the excitation energy decreases, which accelerates a valence change and results in a cooperative phenomenon. They succeeded in explaining the rapid thermal variation of the Eu valence for $EuPd_2Si_2$. They also pointed out a possibility of a first-order transition in the framework of the ICF model with taking an appropriate value of α. This was directly demonstrated by Felner and Nowik, when they applied the ICF model to $YbInCu_4$.[11] In the following, we discuss the temperature- and field-induced valence transition of the $Eu(Pd_{1-x}Pt_x)_2Si_2$ system on the basis of this model. The temperature dependence of p_2 can be calculated by solving Eqs. (1) and (2). The solutions were obtained by iterations starting with two initial values, $p_2 = 1$ and $p_2 = 0$. For simplicity, the excited spin-orbit states of Eu^{3+} [the second- and higher-order terms in the denominator of Eq. (1)] were neglected. The results for various α values are shown in Fig. 10 with $E_0 = 600$ K and $T_f = 50$ K. The equations have two solutions for $\alpha = 1.1$ in the intermediate temperature range, suggesting the occurrence of a first-order phase transition, while the curve for $\alpha = 0.6$ indicates a continuous transition. Croft *et al.* obtained $\alpha = 0.93$ for $EuPd_2Si_2$ from the analyses of the temperature dependence of the isomer shift.[16] This value is just below the critical value for the occurrence of a first-order valence transition. The smaller α value makes the valence transition more gradual.

In the presence of a magnetic field, the Eu^{2+} energy level is split into eight levels due to the Zeeman energy. Then, the equations to be solved are given by

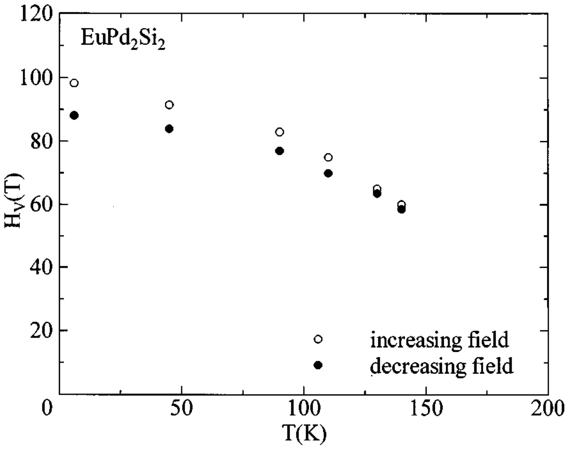

FIG. 8. Temperature dependence of H_V of $EuPd_2Si_2$.

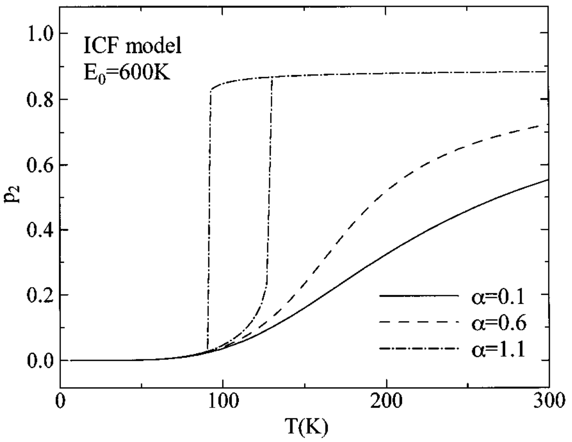

FIG. 10. Temperature dependence of the occupation probability of Eu^{2+}, p_2 calculated from ICF model with several values of α.

$$\frac{p_2}{p_3}=\sum_{J_z=-7/2}^{7/2}\exp(-E_{\rm ex}/kT^*), \tag{3}$$

$$E_{\rm ex}=E_0(1-\alpha p_2)+g\mu_B J_z H, \tag{4}$$

where $g=2$ for Eu^{2+} and the excited states for Eu^{3+} are neglected. The field dependence of p_2 was calculated for $\alpha=1.1$, 0.6, and 0.1 at $T=0$ K. The calculated results are shown in Fig. 11. The parameters E_0 and T_f are the same as before. The curve for $\alpha=1.1$ indicates a first-order metamagnetic transition. This corresponds to the YbInCu$_4$ case, in which a first-order phase transition is induced by both temperature and magnetic field. More realistic calculations have been performed by Nowik *et al.* for the magnetization curve of YbInCu$_4$ at 40 K.[17] A surprising result is the curve for $\alpha=0.6$, where a first-order phase transition takes place with a hysteresis, while the temperature-induced transition is continuous. This is just the EuPd$_2$Si$_2$ case, as revealed by the present experiments. This is due to the fact that the excitation energy is strongly affected by the magnetic field. Since the Eu^{2+} state is free from the crystal field effects, the Zeeman energy gain of the lowest energy level equals $7\mu_B$H. This energy gain is about 470 K at $H=100$ T, being comparable to the E_0 value that we used. A rapid decrease of the excitation energy by magnetic field increases p_2, which gives a positive feedback on $E_{\rm ex}$, leading to a cooperative sharp transition. On the other hand, the valence changes continuously with increasing magnetic field for $\alpha=0.1$. Figure 12 shows the p_2 vs H curves for $\alpha=0.6$ at several temperatures. The curve at $T=60$ K still shows a first-order phase transition but its hysteresis is quite narrow. No abrupt change of the valence is observed at $T=120$ K. As temperature is increased, the mean transition field decreases. These results are qualitatively in agreement with the observed results.

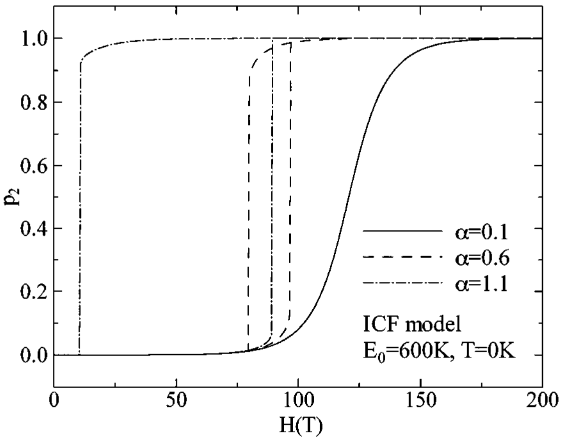

FIG. 11. Calculated results of p_2 as a function of magnetic field for $\alpha=0.1$, 0.6, and 1.1 at $T=0$ K.

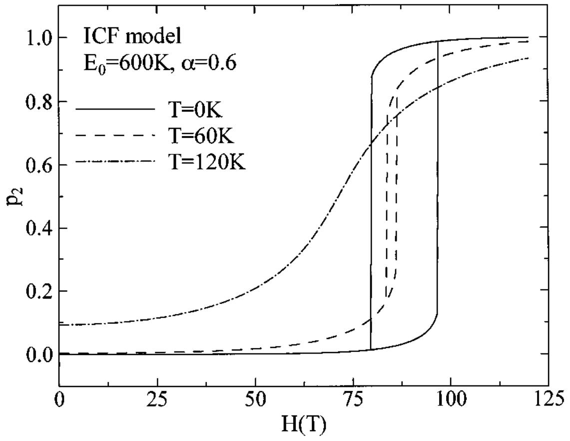

FIG. 12. Field dependence of p_2 calculated from the ICF model at several temperatures.

Finally, we point out a factor determining T_V in Eu(Pd$_{1-x}M_x$)$_2$Si$_2$ (M = Au, Pt). Since a divalent state has larger volume than a trivalent state in Eu, lattice expansion stabilizes a divalent state. However, no simple relation has been obtained between T_V and the volume or the lattice parameters for above systems. We found that T_V scales to the Eu-Pd distance $d_{\text{Eu-Pd}}$, as shown in Fig. 13. One sees that the data of Eu(Pd$_{1-x}$Pt$_x$)$_2$Si$_2$ and Eu(Pd$_{1-y}$Au$_y$)$_2$Si$_2$ lie on a universal line. These results suggest that the Eu-Pd distance plays a crucial role in determining T_V in these systems.

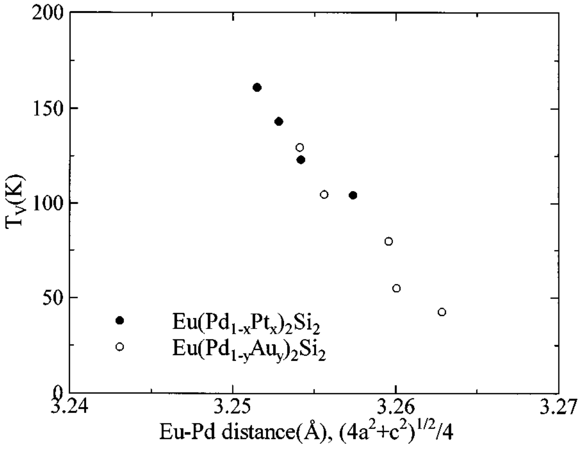

FIG. 13. Plots of the transition temperature T_V vs Eu-Pd distance $d_{\text{Eu-Pd}}$, $\sqrt{4a^2+c^2}/4$, of Eu(Pd$_{1-x}$Pt$_x$)$_2$Si$_2$ and Eu(Pd$_{1-y}$Au$_y$)$_2$Si$_2$. Data of Eu(Pd$_{1-y}$Au$_y$)$_2$Si$_2$ were taken from Refs. 5 and 18.

V. CONCLUSION

We have observed a field-induced metamagnetic transition in $Eu(Pd_{1-x}Pt_x)_2Si_2$ with $0 \leqslant x \leqslant 0.15$. The metamagentic transition is of first order with a large hysteresis. The metamagnetic transition field H_V as well as the valence transition temperature T_V decreases with increasing the Pt content. A linear relation between H_V and T_V is observed for the present system, similarly to the $YbIn_{1-x}Ag_xCu_4$ system. A satisfying description has been provided for the field-induced valence transition by the ICF model, by taking into account the p_2 dependence of the excitation energy. Especially, we have demonstrated that *a first-order valence transition could be induced by magnetic field, even if the system shows a continuous valence transition against temperature.* The temperature dependence of H_V is qualitatively explained by the present model. For further quantitative discussion, the temperature dependence of the mean valence has to be evaluated. From this point of view, the L_{III}-XAS experiments on $Eu(Pd_{1-x}Pt_x)_2Si_2$ are in progress.

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