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First-Order Valence Transition of $EuPd_2Si_2$ Induced by High Magnetic Fields

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In order to study the magnetic field effects on the intermediate valence of the Eu system, magnetization was measured for $EuPd_2Si_2$ and $Eu(Pd_{0.95}Pt_{0.05})_2Si_2$ up to 100 T. A first-order metamagnetic transition was observed for both samples under high magnetic fields. The transition field is 93T for $EuPd_2Si_2$ at 6 K. The saturation magnetization close to $7\mu_B$ indicates that this metamagnetism is a field-induced valence transition from an intermediate valence state to a divalent state of the Eu ion. Based on the interconfigurational fluctuation (ICF) model, the excitation energy to convert an Eu^{3+} ion into Eu^{2+} was estimated. Temperature dependence of the metamagnetic transition field of $EuPd_2Si_2$ was also studied.

KEYWORDS: intermediate valence, $EuPd_2Si_2$, high field, metamagnetism

A variety of exotic phenomena have been found in rare-earth compounds, such as intermediate valence, dense Kondo effect and heavy fermion behavior. Some Eu-based compounds show intermediate valence between Eu^{2+} ($4f^7$) and Eu^{3+} ($4f^6$) configurations. An important feature of Eu systems is that they exhibit a strongly temperature-dependent valence. Typical examples are EuM_2Si_2 (M = Cu, Pd and Ir) compounds with the $ThCr_2Si_2$ tetragonal structure.[1-3] In these systems, the Eu atom is in a nearly trivalent state at low temperatures and it shifts toward Eu^{2+} with increasing temperature. Among them, $EuPd_2Si_2$ undergoes a precipitous, yet continuous, valence change at around 150 K.[2] Various kinds of measurements, such as susceptibility, Mössbauer effect and X-ray absorption, have revealed that the Eu valence changes from 2.8 at $T = 130$ K to 2.3 at $T = 180$ K. Due to a substantial size difference between Eu^{2+} and Eu^{3+} ions, the Eu valence is also sensitive to pressure. Applying pressure destabilizes a divalent state. Abd-Elmeguid *et al.* have studied the pressure effects on Mössbauer spectra of antiferromagnetic $Eu(Pd_{0.8}Au_{0.2})_2Si_2$.[4] They found that the mean valence of this compound changes from 2.0 to 2.6 under 30 kbar at 4.2 K, accompanied by a collapse of the antiferromagnetic order.

The Eu^{2+} ($4f^7$) configuration has a high magnetic moment with $J = 7/2$, $7\mu_B$, while the Eu^{3+} ($4f^6$) configuration is in a nonmagnetic state with $J = 0$. These suggest that the mean valence might be affected by a magnetic field. The magnetic field effects on the Eu valence were first demonstrated by Scherzberg *et al.* on $EuCu_2Si_2$.[5] They observed the valence shift of $\Delta v = 0.015$ induced by a magnetic field of 12.8 T at 150 K. If the Zeeman energy gain is larger than the energy difference between Eu^{2+} and Eu^{3+} states, the divalent state is stabilized under high magnetic fields, giving rise to a substantial magnetization. This phenomenon can be called a field-induced valence transition. Such a transition was observed in $YbInCu_4$[6] and related compounds,[7] but no work has been reported for Eu compounds.

Recent developments in high-field generation have enabled us to measure the magnetization under ultra-high magnetic field of 100 T. In this paper, we present the results of magnetic field effects on the Eu valence of $EuPd_2Si_2$. As described later, we have succeeded in the observations of a field-induced valence transition of this compound for the first time.

The samples of $EuPd_2Si_2$ and $Eu(Pd_{0.95}Pt_{0.05})_2Si_2$ were synthesized by arc melting the constituent elements with purities better than 99.9% under purified argon atmosphere. The latter sample was prepared in order to lower the valence transition temperature of $EuPd_2Si_2$, because $EuPt_2Si_2$ is a divalent antiferromagnet.[8] The ingots were subsequently annealed at 800°C for one week in an evacuated quartz tube. The X-ray diffraction patterns have shown that the samples have a single phase with the $ThCr_2Si_2$ structure. The magnetic susceptibility was measured by a Faraday method. High magnetic fields up to 100 T were generated by means of a fast capacitor discharge into a destructive single-turn coil. The duration time of the pulsed field was about 7μs. The magnetization processes were measured by an induction method with well-balanced pick-up coils. To avoid eddy current effects, powder samples were used for measurements.

Figure 1 shows the temperature dependence of the inverse susceptibility of $EuPd_2Si_2$ and $Eu(Pd_{0.95}Pt_{0.05})_2Si_2$. At higher temperatures above 200 K, the Curie-Weiss susceptibility is observed for both compounds. On cooling, χ strongly deviates from the Curie-Weiss behavior below 170 K for $EuPd_2Si_2$, where a continuous va-

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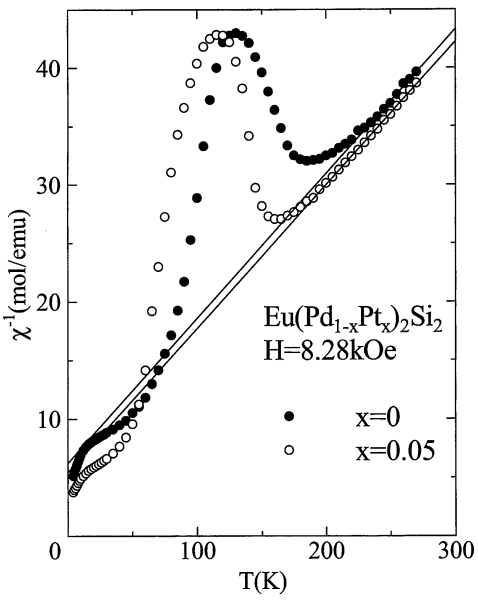

Fig. 1. Temperature dependence of the inverse susceptibility of $EuPd_2Si_2$ and $Eu(Pd_{0.95}Pt_{0.05})_2Si_2$. Solid lines show the Curie-Weiss law.

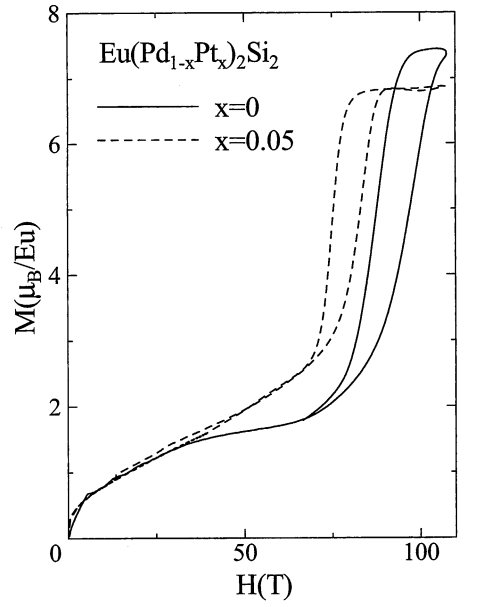

Fig. 2. High-field magnetization curves of $EuPd_2Si_2$ and $Eu(Pd_{0.95}Pt_{0.05})_2Si_2$ at 6 K.

lence transition takes place. Similar deviation of χ from the Curie-Weiss law is observed below 150 K for the Pt-substituted sample. These results indicate that the substitution of Pt for Pd is effective for lowering the valence transition temperature, as expected. At low temperatures, χ^{-1} again follows the Curie-Weiss law. However, this is not intrinsic but due to a ferromagnetic impurity phase, as several authors have pointed out.[9,10]

High-field magnetization curves of $EuPd_2Si_2$ and $Eu(Pd_{0.95}Pt_{0.05})_2Si_2$ measured at 6 K are shown in Fig. 2. Both samples show a sharp metamagnetic transition under high fields with a large hysteresis of 10 T.

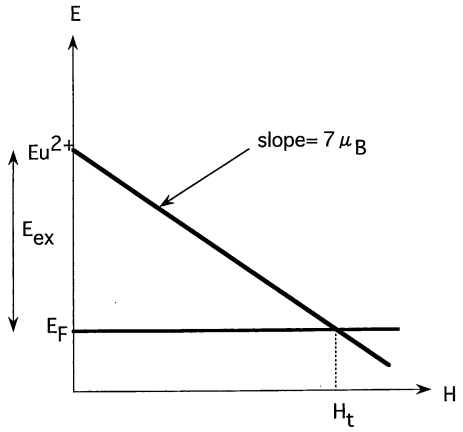

Fig. 3. Energy level scheme of $EuPd_2Si_2$ under magnetic field.

The transition field, H_t (the average value of increasing and decreasing field process), of $EuPd_2Si_2$ and of the 5% Pt sample is 93 T and 80 T, respectively. The metamagnetic transition of $EuPd_2Si_2$ is not completed even at the highest field that we studied, whereas the magnetization of the 5% Pt sample is saturated above 90 T. The saturation magnetization is about $7\mu_B$/Eu, which is in agreement with the theoretical value of 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. The observed large hysteresis in the magnetization curves indicates that the metamagnetic transition is of first order, which is in contrast to the continuous valence change driven by temperature.

So far, the intermediate valence phenomena of the Eu systems have been discussed on the basis of the interconfigurational fluctuation (ICF) model.[11,12] In this model, the occupation probability of the Eu^{2+} state, p_2, and that of Eu^{3+}, p_3, follow Boltzmann statistics,

$$\frac{p_2}{p_3} = \frac{8\exp(-E_{ex}/T^*)}{1+3\exp(-480/T^*)+5\exp(-1330/T^*),} \quad (1)$$

where E_{ex} is the excitation energy required to convert an Eu^{3+} ion into Eu^{2+}, i.e., the energy necessary to take one electron from the conduction band and put it into a 4f level. T^* is an effective temperature defined as $T^* = \sqrt{T^2+T_f^2}$, where T_f is a quantity which represents a broadening of each 4f level. The temperature dependence of the isomer shift and the susceptibility of $EuPd_2Si_2$ have been analyzed in terms of the ICF model by taking E_{ex} and T_f as free parameters.[2,11] We point out that E_{ex} can be estimated directly from H_t, because the metamagnetic transition takes place when the Zeeman energy gain equals the excitation energy: $gJ\mu_B H_t = E_{ex}$. This is illustrated in Fig. 3, where the energy level scheme is given as a function of magnetic field. Fortunately, the divalent state of Eu is free from crystal field effects, therefore, the Zeeman energy gain shows linearlity with the applied field with a slope of $7\mu_B$ ($J = 7/2$ and $g = 2$). The estimated excitation energy is 437 K for $EuPd_2Si_2$. This value is comparable to those estimated from the temperature dependence of

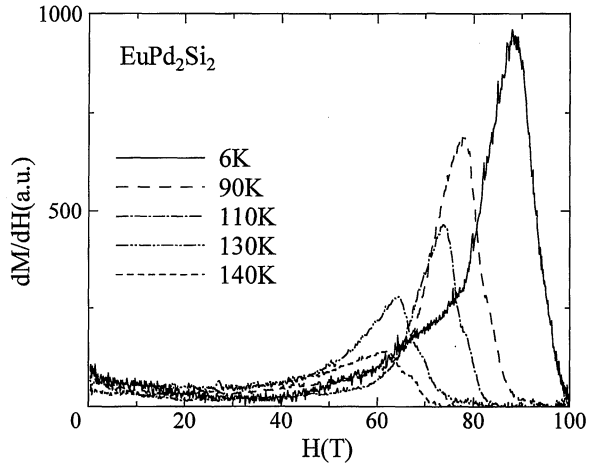

Fig. 4. Differential susceptibility vs magnetic field of $EuPd_2Si_2$ at various temperatures. Data in the decreasing field process are plotted.

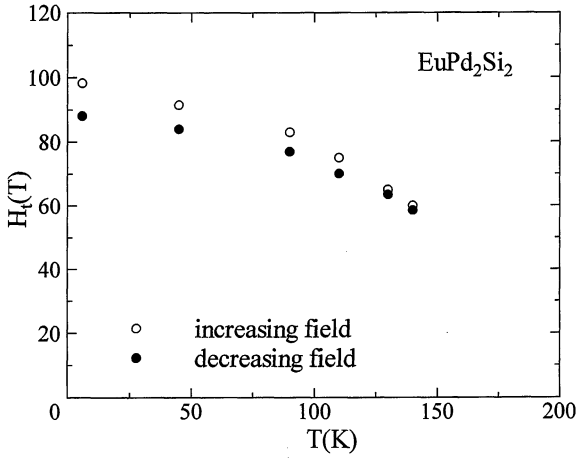

Fig. 5. Temperature dependence of the metamagnetic transition field, H_t of $EuPd_2Si_2$. Open circles: H_t in the increasing field process; closed circles: the decreasing field process.

the isomer shift, 587 K (at 0 K) by Croft *et al.*[11] and 500 K (at 100 K) by Schmiester *et al.*[13] In the present model, E_{ex} is assumed to be independent of p_2 or volume. In the framework of the ICF model, a rapid thermal variation of the valence in $EuPd_2Si_2$ cannot be explained without assuming that E_{ex} is a function of p_2, as $E_{ex} = E_0(1 - \alpha p_2)$.[11-13] Here, E_0 and α are constants and $\alpha > 0$. If the p_2 dependence of E_{ex} is taken into consideration, analyses of the isomer shift give values close to E_0 below 150 K, where $p_2 \simeq 0$. On the other hand, our results give a smaller value of $E_0(1 - \alpha)$, because $p_2 = 1$ after the metamagnetic transition. This is consistent with the observed results.

Figure 4 shows the differential susceptibility vs field of $EuPd_2Si_2$ at various temperatures. Data in the decreasing field process were plotted. Sharp peaks are visible below 110 K, indicating that the compound undergoes a well-defined metamagnetic transition in this temperature range. The metamagnetic transition field decreases with increasing temperature. Above 110 K, the peak is rapidly broadened and it almost vanishes at 140 K. These results suggest that the metamagnetic transition is smeared as the temperature approaches the valence transition point. The temperature dependence of H_t for $EuPd_2Si_2$ is shown in Fig. 5. The transition field shows a Brillouin function-type temperature dependence. Such temperature dependence of H_t is also observed in an other field-induced valence transition system, $YbInCu_4$.[7] These results indicate that E_{ex} decreases smoothly with increasing temperature.

In conclusion, we have observed a metamagnetic transition from an intermediate valence state to a divalent state for $EuPd_2Si_2$ and $Eu(Pd_{0.95}Pt_{0.05})_2Si_2$. The transition is of first order, in contrast to a continuous valence change driven by temperature. Based on the ICF model, the excitation energy, E_{ex} was estimated to be 437 K for $EuPd_2Si_2$ at $T = 6$ K. We emphasize that the observation of the metamagnetic transition is effective to estimate E_{ex} directly in the intermediate valence systems.

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