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# Temperature- and field-induced valence transitions of $\text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2$

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**Abstract.** The magnetic properties of the  $\text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2$  system were studied in which an intermediate-valence state of Eu is realized at around  $x = 0.75$ . It was found that the compounds with  $0.70 \leq x \leq 0.82$  show a temperature-induced valence transition below room temperature, while those with  $x \geq 0.85$  are antiferromagnetic with a stable  $\text{Eu}^{2+}$  state. A first-order valence transition induced by high magnetic field was observed for  $0.75 \leq x \leq 0.82$ . Such valence transitions against temperature or field are discussed on the basis of the interconfigurational fluctuation (ICF) model. It is shown that the observed linear relation between the transition field and the transition temperature is explained by the present model.

## 1. Introduction

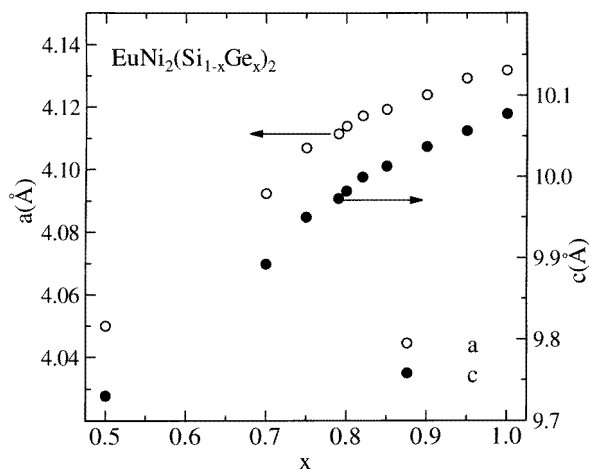
Valence instability of 4f electron systems has been of considerable interest. Among the intermediate-valence systems, Eu compounds are known to exhibit strong temperature dependence of the mean valence. The intermediate-valence state of Eu is realized between  $\text{Eu}^{2+}$  ( $4f^7$ ) and  $\text{Eu}^{3+}$  ( $4f^6$ ) configurations. For example,  $\text{EuPd}_2\text{Si}_2$  undergoes a sharp but continuous valence change from 2.8 to 2.3 at around 160 K (Sampathkumaran *et al* 1981). Various kinds of measurements, such as susceptibility (Sampathkumaran *et al* 1981), Mössbauer effect (Nowik 1983) and x-ray absorption spectroscopy (XAS) measurements (Wortmann 1989), have been applied to estimate the temperature dependence of the valence in Eu compounds.

Pressure and magnetic field are also key parameters as regards causing a valence transition. Due to a large difference in atomic size between  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  ions, the Eu valence is sensitive to pressure. Applying pressure destabilizes a divalent state. This was first demonstrated by Abd-Elmeguid *et al* (1985) for  $\text{Eu}(\text{Pd}_{0.8}\text{Au}_{0.2})_2\text{Si}_2$ . Recently, Hesse and Wortmann (1994) have reported strong nonlinear pressure dependence of the isomer shift in  $\text{EuNi}_2\text{Ge}_2$  and  $\text{EuPd}_2\text{Ge}_2$  at 300 K, suggesting a valence transition from a  $\text{Eu}^{2+}$  to a  $\text{Eu}^{3+}$  state induced by pressure. In contrast to pressure effects, the magnetic field effects on the Eu valence have been less studied, in spite of a large difference in magnetic moment between  $\text{Eu}^{2+}$  ( $7\mu_B$ ) and  $\text{Eu}^{3+}$  (0). Recently, we have examined high-field magnetization processes of  $\text{EuPd}_2\text{Si}_2$  by using a destructive single-turn coil, and observed a sharp metamagnetic

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transition under 93 T at  $T = 6$  K (Wada *et al* 1996). The saturation magnetization close to  $7\mu_B/\text{Eu}$  indicates that the metamagnetic transition is a valence transition from a nearly trivalent state to a divalent one. This is the first example of a field-induced valence transition of Eu-based systems. We have also found that the substitution of Pt for Pd lowers the metamagnetic transition field,  $H_V$ , without broadening the transition (Mitsuda *et al* 1997). A linear relation between  $H_V$  and the valence transition temperature,  $T_V$ , was obtained in the  $\text{Eu}(\text{Pd}_{1-x}\text{Pt}_x)_2\text{Si}_2$  system. However,  $\text{Eu}(\text{Pd}_{1-x}\text{Pt}_x)_2\text{Si}_2$  has a solubility limit with  $x = 0.15$ , and  $H_V$  higher than 65 T makes it difficult to measure various physical properties associated with a field-induced valence transition. It is required to search for another system, which shows temperature- and field-induced valence transitions.

In this paper, we will report that  $\text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2$  shows a field-induced valence transition as well as the temperature-induced valence transition at around  $x = 0.80$ . The Eu ions are trivalent for  $x = 0$  ( $\text{EuNi}_2\text{Si}_2$ ) and divalent for  $x = 1$  ( $\text{EuNi}_2\text{Ge}_2$ ) (Felner and Nowik 1977). Wortmann *et al* (1991) examined the magnetic properties of this system and found that the compound with  $x = 0.75$  shows a strongly temperature-dependent valence. On the basis of their results, we have studied the temperature and field dependence of the magnetization of the compounds with  $0.50 \leq x \leq 0.95$ .

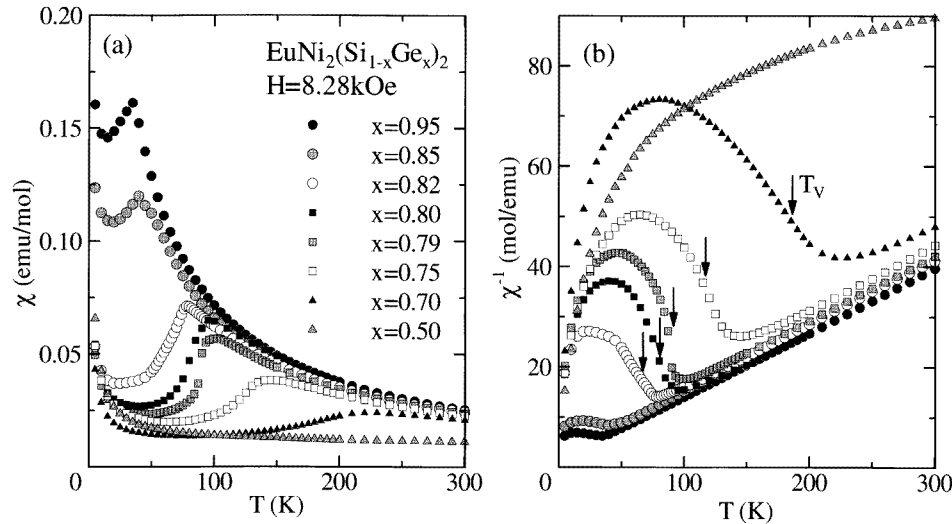


**Figure 1.** The lattice parameters  $a$  and  $c$  of  $\text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2$  with  $0.50 \leq x \leq 1.0$  as functions of  $x$ .

## 2. Experiments

Samples were prepared by melting stoichiometric amounts of the constituent elements in an argon arc furnace. The ingots with  $x \leq 0.70$  and  $x \geq 0.85$  were annealed in an evacuated quartz tube at  $800^\circ\text{C}$  for one week. For  $0.70 < x < 0.85$ , as-cast samples were used for measurements, because as-cast samples showed a sharper valence transition against temperature than annealed ones. All of the samples were confirmed by x-ray diffraction to have a single phase, with the  $\text{ThCr}_2\text{Si}_2$ -type structure. Figure 1 shows the concentration dependence of the lattice parameters  $a$  and  $c$  of  $\text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2$ . Both  $a$  and  $c$  increase with increasing  $x$ . The magnetic susceptibility was measured by means of a SQUID at a constant magnetic field of 8.28 kOe from 4.2 to 300 K. The high-field magnetization was

measured using an induction method with well-balanced pick-up coils. The magnetic field was generated by a capacitor discharge into either a pulsed magnet (43 T) or a destructive single-turn coil (80 T). The XAS measurements at the Eu  $L_{\text{III}}$  edge were carried out on the compounds with  $x = 0.79$  and  $0.82$  at the BL-7C beamline of the KEK Photon Factory using a Si(111) monochromator from 10 to 290 K.

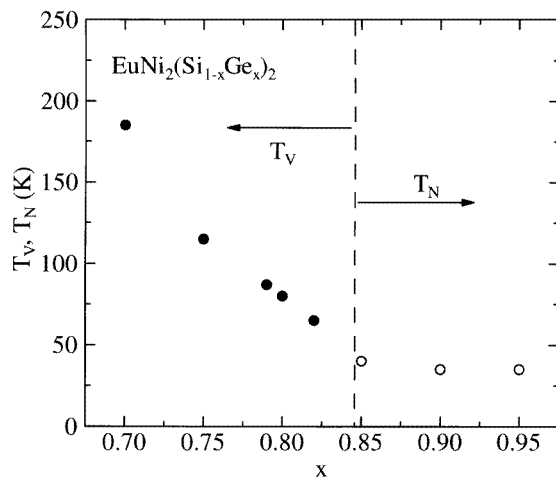


**Figure 2.** (a) The temperature dependence of the magnetic susceptibility  $\chi$  of  $\text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2$ . (b) The temperature dependence of the inverse susceptibility of  $\text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2$ . Arrows indicate the valence transition temperature defined as the inflexion point in the  $\chi$  versus  $T$  curves.

### 3. Results

Figure 2(a) shows the temperature dependence of the magnetic susceptibility of  $\text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2$  with  $0.50 \leq x \leq 0.95$ . The compound with  $x = 0.50$  shows nearly temperature-independent susceptibility, while  $\chi$  is temperature dependent with a maximum at low temperatures for  $x \geq 0.70$ . A rapid rise in the  $\chi$ - $T$  curves for all of the samples at very low temperatures is probably due to an impurity phase containing paramagnetic  $\text{Eu}^{2+}$  moments. The inverse susceptibility versus temperature curves are shown in figure 2(b). For  $0.70 \leq x \leq 0.82$ ,  $\chi$  shows the Curie-Weiss behaviour at higher temperatures, while it deviates substantially from the Curie-Weiss law below a certain temperature. These anomalies are associated with a valence transition, as reported by Wortmann *et al* (1991) for  $x = 0.75$ . This is supported by the results of the XAS measurements, as described later. As seen in figure 2(a), a drop in  $\chi$  is prominent with increasing  $x$  up to  $x = 0.82$ . For  $x = 0.79$ , the susceptibility shows a distinct jump at 85 K, suggesting a first-order valence transition. This was directly confirmed by the temperature dependence of the lattice parameters (Wada 1997). We define the valence transition temperature,  $T_V$ , as an inflexion point in the  $\chi$ - $T$  curves, which is shown by arrows in figure 2(b). On the other hand, the compounds with  $x = 0.85$  and  $0.95$  show a cusp in the  $\chi$ - $T$  curve, which is characteristic of an antiferromagnetic transition. We have studied the transport properties and thermal expansion of  $\text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2$ , and no indication of valence change was detected in the

temperature variation for  $x \geq 0.85$  (Wada 1997). Therefore, the divalent state is stable over the whole temperature range, and the susceptibility peak is due to the Néel order of the  $\text{Eu}^{2+}$  moments for  $x \geq 0.85$ .



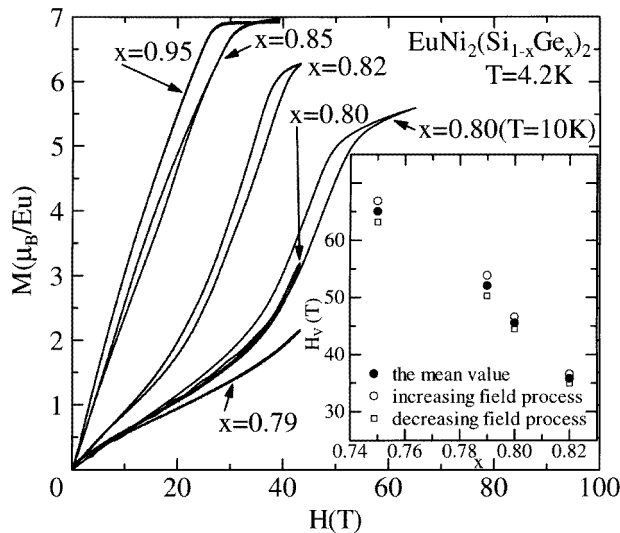
**Figure 3.** The concentration dependence the valence transition temperature  $T_V$  (closed circles) and the Néel temperature (open circles) of  $\text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2$ .

**Table 1.** Values of the effective magnetic moment  $\mu_{\text{eff}}$ , Weiss temperature  $\Theta_p$ , valence transition temperature  $T_V$ , Néel temperature  $T_N$ , and valence transition field  $H_V$  for  $\text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2$ .

$x$	$\mu_{\text{eff}}$ ( $\mu_B/\text{Eu}$ )	$\Theta_p$ (K)	$T_V$ (K)	$T_N$ (K)	$H_V$ (T)
0.75	7.88	-41.5	115		65
0.79	7.92	-29.4	87		52
0.80	7.84	-20.9	80		46
0.82	7.94	-25.5	65		36
0.85	7.78	-14.4		40	
0.90	7.90	-12.6		35	
0.95	7.94	-10.2		35	

The concentration dependence of  $T_V$  and  $T_N$  is shown in figure 3. The valence transition temperature decreases nearly linearly with increasing  $x$  up to  $x = 0.82$ , whereas  $T_N$  is less sensitive to  $x$  in the concentration range of  $x \geq 0.85$ . The effective magnetic moment,  $\mu_{\text{eff}}$ , and the Weiss temperature,  $\Theta_p$  are listed in table 1 together with  $T_N$  or  $T_V$ . The effective moment is 7.78–7.94  $\mu_B/\text{Eu}$ , which is close to the theoretical value for  $\text{Eu}^{2+}$ , 7.94 $\mu_B$ . The Weiss temperature is negative and its absolute value decreases with increasing  $x$ .

The magnetization curves of  $\text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2$  at 4.2 K up to 43 T are displayed in figure 4. The compound with  $x = 0.82$  shows a metamagnetic transition with a large hysteresis, which originates in the valence transition. The magnetization curves for  $x = 0.79$  and 0.80 also show an indication of the metamagnetic transition at the highest field. The magnetization process was examined up to 80 T for  $0.70 \leq x \leq 0.80$ . A clear metamagnetic transition was observed for the compounds with  $0.75 \leq x \leq 0.80$ . An example of a magnetization curve for  $x = 0.80$  up to 80 T at 10 K is shown in figure 4. On the other hand, the magnetization for  $x = 0.95$  increases nearly linearly with increasing field, eventually



**Figure 4.** Magnetization curves of  $\text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2$  up to 43 T at  $T = 4.2$  K. The high-field magnetization curve up to 80 T at  $T = 10$  K is also shown for  $x = 0.80$ . The inset shows the concentration dependence of the valence transition field  $H_V$ . Data for the increasing-field process (open circles), and the decreasing-field process (open squares), and the mean value (closed circles) are plotted.

reaching a saturation value of about  $7\mu_B$ . This behaviour is explained as the magnetization process of an antiferromagnet with a small magnetic anisotropy. The magnetization curve for  $x = 0.85$  is similar to that for  $x = 0.95$ , but a small hysteresis accompanies it. These results suggest that most of the Eu atoms are in the divalent state, and a small proportion of them in the nearly trivalent state due to concentration fluctuations shows a metamagnetic valence transition in this sample. The valence transition field,  $H_V$ , is obtained from the peak position in the  $dM/dH$  versus  $H$  curves. The concentration dependence of  $H_V$  is shown in the inset of figure 4. Data for both increasing-field and decreasing-field processes are plotted, as well as the mean value. The mean value of  $H_V$  is also listed in table 1. The transition field decreases with increasing  $x$ . The hysteresis width also decreases as the Ge content approaches the critical boundary for  $x = 0.82$ .

The x-ray absorption spectra at the Eu  $L_{\text{III}}$  edge for  $x = 0.79$  at various temperatures are shown in figure 5. At any temperature, the spectrum can be decomposed into two subspectra, the  $(2p^54f^75d^*)$  and  $(2p^54f^65d^*)$  final-state components. These are direct evidence of the intermediate-valence phenomena of the present compounds. Similarly to the results for  $x = 0.75$  reported by Wortmann *et al* (1991), their relative intensities are strongly dependent on temperature. The data were analysed in the standard procedure using two sets of  $L_{\text{III}}$ -edge profiles, each of which consists of an arctangent function and a Lorentzian, and the mean valence is evaluated from the relative intensities of the two components (Wortmann 1989). Here, so-called final-state effects were taken into consideration, and the mean valence is corrected according to Wortmann *et al* (1991). The mean valence for  $x = 0.79$  and 0.82 is shown in figure 6 as a function of temperature. For both compounds, the mean valence is about 2.8 in the ground state, while it decreases rapidly with increasing temperature and reaches a constant value of about 2.3 above 200 K. The midpoints of the valence change are in agreement with  $T_V$  determined by the susceptibility measurements.

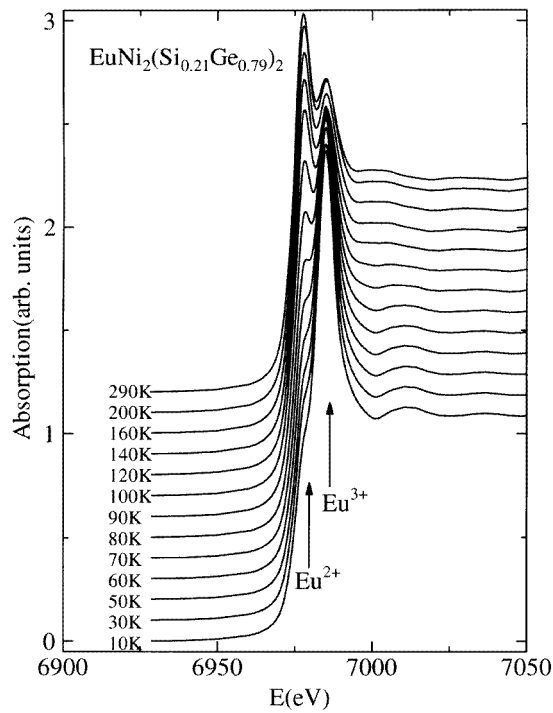


Figure 5. X-ray absorption spectra at the Eu L<sub>III</sub> edge for  $x = 0.79$  at various temperatures.

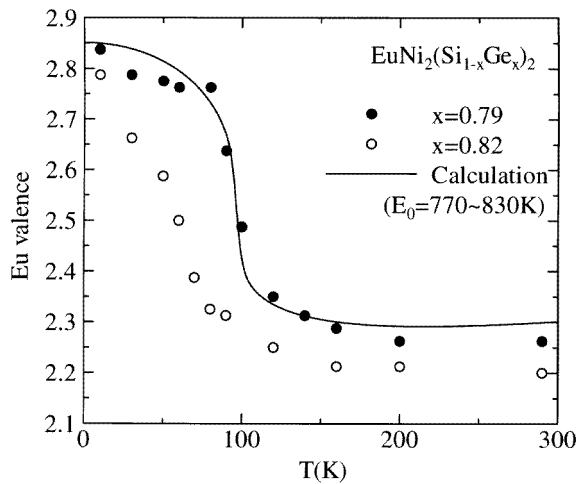
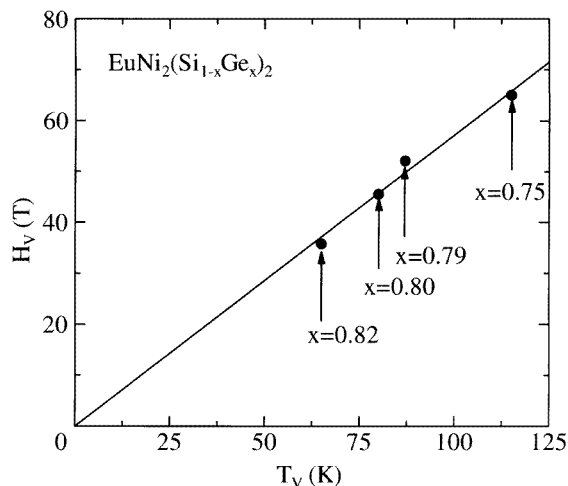


Figure 6. The temperature dependence of the mean valence for  $x = 0.79$  and  $0.82$  estimated from XAS. The solid line for  $x = 0.79$  is the  $v$  versus  $T$  curve calculated by means of the ICF model with  $\alpha = 1.05$ ,  $p_2(0) = 0.15$ , and  $E_0 = 770\text{--}830$  K.

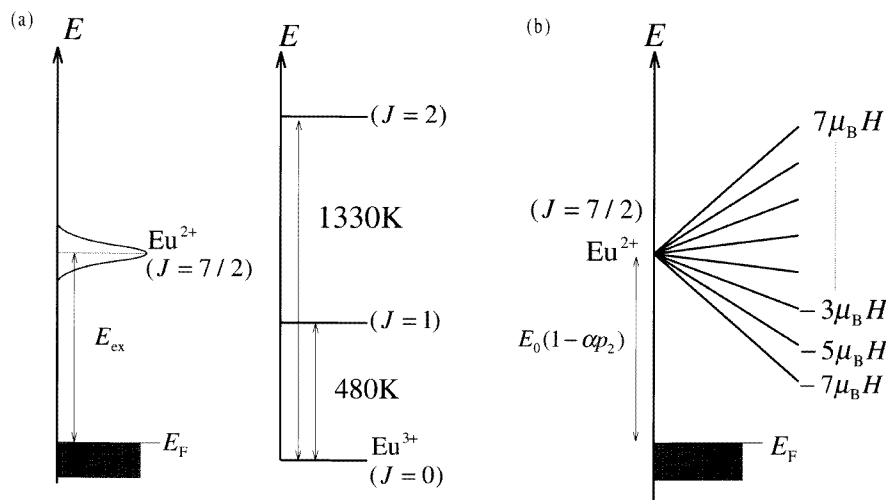
#### 4. Discussion

The present study has revealed that the  $\text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2$  system shows a field-induced valence transition as well as the temperature-induced valence transition at around  $x = 0.80$ ,



**Figure 7.**  $H_V$  versus  $T_V$  plots for  $\text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2$ . The solid line is a guide to the eye.

similarly to  $\text{Eu}(\text{Pd}_{1-x}\text{Pt}_x)_2\text{Si}_2$ . In the case of  $\text{Eu}(\text{Pd}_{1-x}\text{Pt}_x)_2\text{Si}_2$ , a linear relation was observed between  $H_V$  and  $T_V$  (Mitsuda *et al* 1997). The plots of  $H_V$  versus  $T_V$  for  $\text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2$  are shown in figure 7. It is seen that  $H_V$  is proportional to  $T_V$  for the present system as well as for  $\text{Eu}(\text{Pd}_{1-x}\text{Pt}_x)_2\text{Si}_2$ . Furthermore, the slope of the plot is  $0.572 \text{ T K}^{-1}$ , which is close to that of  $\text{Eu}(\text{Pd}_{1-x}\text{Pt}_x)_2\text{Si}_2$ , namely  $0.568 \text{ T K}^{-1}$  (Mitsuda *et al* 1997). These results suggest that a linear relation between  $H_V$  and  $T_V$  is universal in the field-induced valence transition systems of Eu-based compounds.



**Figure 8.** (a) The energy level scheme for Eu in the intermediate state proposed on the basis of the ICF model. (b) The energy level scheme for a  $\text{Eu}^{2+}$  state under a magnetic field of  $H$ .

In a previous paper, we discussed the field-induced valence transition on the basis of the interconfigurational fluctuation (ICF) model (Mitsuda *et al* 1997). In the following, we briefly summarize the main points of the discussion. Assuming a trivalent state as a ground



state, the occupation probabilities of the  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  states, represented as  $p_2$  and  $p_3$ , respectively, are given by Boltzmann statistics (Sales and Wohleben 1975, Nowik 1983):

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

where  $p_2 + p_3 = 1$  and  $E_{\text{ex}}$  is the excitation energy required to convert a  $\text{Eu}^{3+}$  configuration into a  $\text{Eu}^{2+}$  one, i.e. the energy necessary to take one electron from the conduction band and put it into a 4f level. The energy level scheme is illustrated in figure 8(a). And  $T^*$  is the effective temperature defined as

$$T^* = \sqrt{T^2 + T_f^2}$$

where  $T_f$  is a quantity which allows a broadening of each 4f level. The mean valence,  $v$ , is given by  $v = 3 - p_2$ . A simple ICF model, however, is insufficient for describing a rapid thermal variation of the mean valence of  $\text{EuPd}_2\text{Si}_2$ . Such a sharp valence change is interpreted as a cooperative phenomenon, and has been discussed by assuming a  $p_2$ -dependence of the excitation energy as follows (Croft *et al* 1982):

$$E_{\text{ex}} = E_0(1 - \alpha p_2) \quad (2)$$

where  $E_0$  and  $\alpha$  are parameters. The mean valence,  $v$ , or  $p_2$  is obtained by solving equations (1) and (2) self-consistently as a function of temperature, when  $E_0$ ,  $\alpha$ , and  $T_f$  are given. The nature of the valence transition is sensitive to  $E_0$  and  $\alpha$ . Keeping  $E_0$  constant, the temperature dependence of the valence change becomes sharper with increasing  $\alpha$ , and a first-order valence transition takes place when  $\alpha$  exceeds a certain critical value (Felner and Nowik 1986, Mitsuda *et al* 1997). In the presence of a magnetic field, the eightfold degeneracy of the  $\text{Eu}^{2+}$  energy level is lifted due to the Zeeman energy. This is schematically illustrated in figure 8(b). The excited states of the  $\text{Eu}^{3+}$  level are also split by the magnetic field. Thus, the occupation probabilities are given by

$$\begin{aligned} \frac{p_2}{p_3} = & \left( \sum_{J_z=-7/2}^{7/2} \exp\{[-E_0(1 - \alpha p_2) + g_2 \mu_B J_z H]/kT^*\} \right) \\ & \times \left( 1 + \sum_{J_z=-1}^1 \exp[(-480k + g_3 \mu_B J_z H)/kT^*] \right. \\ & \left. + \sum_{J_z=-2}^2 \exp[(-1330k + g_3 \mu_B J_z H)/kT^*] \right)^{-1} \end{aligned} \quad (3)$$

where  $g_2$  and  $g_3$  are the Landé  $g$ -factors of  $\text{Eu}^{2+}$  (2) and  $\text{Eu}^{3+}$  (3/2), respectively. By choosing appropriate parameters  $E_0$  and  $\alpha$ , we have shown that a first-order valence transition is induced by high magnetic fields (Mitsuda *et al* 1997).

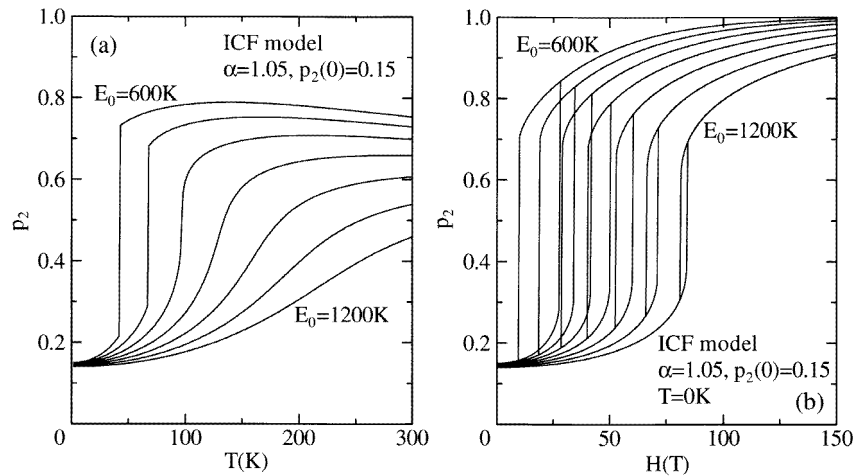
In this paper, we apply the above model to  $\text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2$ , in particular with  $x = 0.79$ . First, we evaluate the parameters  $E_0$ ,  $\alpha$ , and  $T_f$  to reproduce the temperature dependence of the mean valence obtained from the XAS measurements. We assume that  $T_f$  is temperature independent. Putting  $T = 0$  into equation (1), we have

$$\frac{p_2(0)}{1 - p_2(0)} = \frac{8 \exp[-E_0(1 - \alpha p_2(0))/kT_f]}{1 + 3 \exp[-480/T_f]} \quad (4)$$

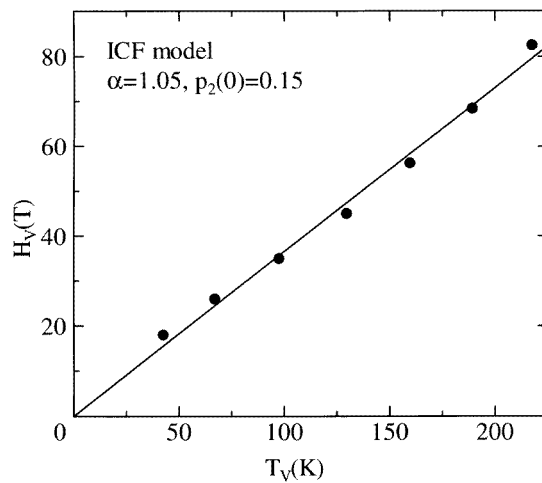
where  $p_2(0)$  is  $p_2$  at  $T = 0$  K, and terms of higher order than  $J = 2$  are neglected in the  $\text{Eu}^{3+}$  state. This equation means that  $T_f$  is not independent when  $E_0$ ,  $\alpha$ , and  $p_2(0)$  are given. From figure 6, we have  $p_2(0) = 0.15$  for  $x = 0.79$ . As mentioned above, the nature of

the valence transition strongly depends upon the parameters  $E_0$  and  $\alpha$ . The results of XAS measurements suggest that the valence changes smoothly against temperature for  $x = 0.79$ . However, it is difficult to observe a first-order valence transition by XAS, because of its short observation time, of the order of  $10^{-15}$  s. Furthermore, a first-order valence transition in inhomogeneous systems would give a smooth temperature variation of the valence as well as a continuous valence change in homogeneous ones. On the other hand, the  $\chi$ - $T$  curve for  $x = 0.79$  exhibits a jump at  $T_V$ , suggesting a first-order phase transition. In order to elucidate this point, we measured the temperature dependence of the lattice parameters for  $x = 0.79$  (Wada 1997). We observed the coexistence of two phases with different lattice parameters between 60 K and 110 K, and their relative intensity ratio changes with increasing temperature. These results indicate that the system undergoes a first-order phase transition but the transition temperature is distributed due to concentration fluctuations. This is consistent with a sharp drop observed in the  $\chi$ - $T$  curve at  $T_V$ . On the basis of these results, we determined the parameters  $E_0$  and  $\alpha$  for  $x = 0.79$ . To reproduce a smooth variation in  $\nu$  versus  $T$  plots, the Gaussian distribution of  $E_0$  was taken into consideration with a constant value of  $\alpha$ . The calculated results are shown in figure 6 by a solid line, with  $\alpha = 1.05$  and  $E_0$  ranging from 770 K to 830 K. The corresponding value of  $T_f$  is in the range 179–195 K. The agreement between the calculated results and the observed ones is satisfactory. The magnetic field dependence of  $p_2$  at  $T = 0$  K was calculated by solving equation (3) self-consistently using the same parameters. The result indicates that a first-order valence transition at about 40 T accompanied with a hysteresis is induced by a magnetic field, which is in agreement with the observed magnetization curve for  $x = 0.80$ . These results suggest the validity of the ICF model for describing the temperature- and field-induced valence transitions of  $\text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2$ . We have also tried to calculate the  $\nu$  versus  $T$  curve for  $x = 0.82$ . However, we did not succeed in reproducing a steep change of  $\nu$  at low temperatures within the present model. This would be due to the inhomogeneity of the Eu valence in the sample. According to the x-ray diffraction measurements at low temperatures, the two phases coexist even at 10 K for  $x = 0.82$ , indicating that a proportion of the Eu atoms are in the divalent state at the lowest temperature. Such inhomogeneity gives rise to local distortion and hence negative pressure on residual Eu atoms, which possibly accelerates the valence transition at lower temperatures compared with the ideal case. In other words, an asymmetric distribution of  $E_0$  or  $\alpha$  might be taken into consideration to explain the temperature dependence of  $\nu$  for  $x = 0.82$ , which is a problem for the future.

Finally, we discuss a couple of features of the valence transition derived from the present model. We have two important parameters,  $E_0$  and  $\alpha$ , which characterize the nature of the valence transition. The valence transition temperature,  $T_V$ , is sensitive to  $E_0$ . In our results,  $T_V$  changes systematically with  $x$ ; therefore, we expect that the Ge concentration is mainly responsible for the change of  $E_0$ . Assuming that  $\alpha = 1.05$  and  $p_2(0) = 0.15$ , we calculated the  $p_2$  versus  $T$  curves with different values of  $E_0$  ranging from 600 K to 1200 K. The results are displayed in figure 9(a). If the valence transition is of first order, the calculated curve shows the thermal hysteresis more or less. In this figure, however, the  $p_2$  versus  $T$  curves were drawn without hysteresis, so the valence transition takes place at the midpoint of the hysteresis. With increasing  $E_0$ , the valence transition temperature increases and the valence change becomes continuous and gradual against temperature. These results are in qualitative agreement with the observed  $\chi$  versus  $T$  curves of  $\text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2$  shown in figure 2(a). For  $x = 0.5$ , we did not detect any sign of the valence change up to room temperature from the  $\chi$  versus  $T$  curve up to room temperature. Wortmann *et al* (1991) observed a considerable shift of the Mössbauer spectra between 400 K and 600 K, suggesting a gradual valence change for  $x = 0.5$  over the wide temperature range above



**Figure 9.** (a) Calculated results for  $p_2$  as a function of temperature with various values of  $E_0$  ranging from 600 K to 1200 K. The parameters  $\alpha$  and  $p_2(0)$  are set to 1.05 and 0.15, respectively. (b) Calculated results for  $p_2$  as a function of magnetic field at  $T = 0$  K obtained using the same parameters as in (a).



**Figure 10.** The relation between  $H_V$  and  $T_V$  obtained from figures 9(a) and 9(b). The solid line is a guide to the eye.

room temperature. Such behaviour would be expected for a value of  $E_0$  larger than 1200 K. The magnetic field dependence of  $p_2$  for various values of  $E_0$  at  $T = 0$  K was calculated by using the same parameters  $\alpha$  and  $p_2(0)$ , and is shown in figure 9(b). As  $E_0$  is increased, the valence transition field,  $H_V$ , increases. From figures 9(a) and 9(b), we obtain an  $H_V$  versus  $T_V$  plot, as shown in figure 10. It is found that  $H_V$  is proportional to  $T_V$ , which is the universal relation for Eu compounds, as mentioned in the first part of this section. These results strongly support the validity of the present model for describing the temperature and field dependence of the valence transitions of Eu systems.

## 5. Conclusions

We have studied the magnetic properties of  $\text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2$ , and reached the following conclusions.

(i) The temperature-induced valence transition was observed in the concentration range  $0.70 \leq x \leq 0.82$  below room temperature. The valence transition becomes sharp with increasing  $x$ . On the other hand, a divalent state was stabilized for  $x > 0.82$ .

(ii) For  $0.75 \leq x \leq 0.82$ , a first-order valence transition was induced by a high magnetic field. The transition field decreases with increasing  $x$ .

(iii) Such valence transitions were discussed on the basis of the ICF model, in which a  $p_2$ -dependence of the excitation energy is taken into consideration. Assuming a Gaussian distribution of the transition temperature, we calculated the temperature variation of the Eu valence, which is in agreement with the experimental results for  $x = 0.79$ .

(iv) A linear relation between  $H_V$  and  $T_V$  was observed for  $\text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2$  as well as for  $\text{Eu}(\text{Pd}_{1-x}\text{Pt}_x)_2\text{Si}_2$ . This relation was obtained in the framework of the present model, by assuming that only  $E_0$  is concentration dependent.

We emphasize that  $\text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2$  is a suitable system in which we can study not only a field-induced valence transition but also a transition process of the Eu valence state with concentration, starting from a pure divalent state to a trivalent one through an intermediate-valence state. From this point of view, measurements on the transport properties and temperature dependence of the lattice parameters are in progress, which will be published elsewhere.

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## References

- Abd-Elmeguid M M, Sauer Ch and Zinn W 1985 *Phys. Rev. Lett.* **55** 2467
- Croft M, Hodges J A, Kemly E, Krishnan A, Murgai V and Gupta L C 1982 *Phys. Rev. Lett.* **48** 826
- Felner I and Nowik I 1977 *J. Phys. Chem. Solids* **39** 763
- 1986 *Phys. Rev. B* **33** 617
- Hesse H J and Wortmann G 1994 *Hyperfine Interact.* **93** 1499
- Mitsuda A, Wada H, Shiga M, Katori H A and Goto T 1997 *Phys. Rev. B* **55** 12474
- Nowik I 1983 *Hyperfine Interact.* **13** 89
- Sales B C and Wohlleben D K 1975 *Phys. Rev. Lett.* **35** 1240
- Sampathkumaran E V, Gupta L C, Vijayaraghavan R, Gopalakrishnan K V, Pillay R G and Devare H G 1981 *J. Phys. C: Solid State Phys.* **14** L237
- Wada H 1997 in preparation
- Wada H, Mitsuda A, Shiga M, Katori H A and Goto T 1996 *J. Phys. Soc. Japan* **65** 3471
- Wortmann G 1989 *Hyperfine Interact.* **47** 179
- Wortmann G, Nowik I, Perscheid B, Kaindl G and Felner I 1991 *Phys. Rev. B* **43** 5261