Pressure Evolution of Characteristic Electronic States in EuRh$_2$Si$_2$ and EuNi$_2$Ge$_2$

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Abstract. EuRh$_2$Si$_2$ and EuNi$_2$Ge$_2$ are known to reveal the valence transition at pressure of about 1 and 2 GPa, respectively, from a divalent state (Eu$^{2+}$) to a nearly Eu-trivalent state (Eu$^{3-5}$). We have succeeded in growing single crystals of EuRh$_2$Si$_2$ by the Bridgman method and EuNi$_2$Ge$_2$ by the In-flux method. In order to clarify the transition of electronic properties from Eu$^{2+}$ to Eu$^{3-5}$ in detail, we carried out electrical resistivity measurements under pressure. EuRh$_2$Si$_2$ indicates a remarkable first-order valence transition in the pressure range from 1 to 2 GPa with a sharp hysteresis in the electrical resistivity. At 2.12 GPa, the temperature dependence of the electrical resistivity exhibit a broad peak, implying a moderate heavy-fermion state such as EuPd$_2$Si$_2$ and EuIr$_2$Si$_2$. While, EuNi$_2$Ge$_2$ indicates a first-order valence transition in the pressure range from 2 to 3.22 GPa with a hysteresis in the electrical resistivity. At 2.8 GPa, the electrical resistivity of EuNi$_2$Ge$_2$ also shows a characteristic behavior for a moderate heavy-fermion compound. Pressure - temperature phase diagrams for both compounds are constructed.

1. Introduction

Eu atoms in a compound exhibit two kinds of valence states with Eu$^{2+}$ ($4f^76s^2$) and Eu$^{3+}$ ($4f^65d^16s^2$). Since Eu$^{2+}$ is magnetic, Eu-compounds with Eu$^{2+}$ state order magnetically at low temperatures due to the Ruderman– Kittel–Kasuya–Yosida interaction. The magnitude of the magnetic moment of Eu$^{2+}$ ion is the same as that of the corresponding Gd$^{3+}$ electronic state ($J = S = 7/2$, $L = 0$), where $J$ is a total angular momentum, $S$ is a spin angular momentum, and $L$ is an orbital angular momentum. On the contrary, the electronic state of Eu$^{3+}$ is non-magnetic, since $J$ becomes zero as a result of $S = L = 3$. Vast majority of Eu compounds, Eu ions are in the divalent electronic state and orders magnetically. Compounds with Eu-trivalent state are small in number compared to the Eu-divalent compounds. It should be noted that the valence state of the Eu ion is changed by external parameters such as element substitution (chemical pressure), temperature, magnetic field, and pressure, owing to the differences in the ionic sizes and magnetic properties between the Eu$^{2+}$ and Eu$^{3+}$ ions.
Figure 1. Electronic properties of EuT$_2$X$_2$ with ThCr$_2$Si$_2$-type tetragonal structure as a function of the lattice parameter along the c-axis. Open square (□) indicates magnetic ordering temperature, open circle (○) indicates a temperature where the electrical resistivity shows broad maximum, and black bar indicates the c-axis lattice parameter of trivalent Eu compounds.

One of the most systematically studied Eu compounds is a EuT$_2$X$_2$ (T: transition metal, X: Si, Ge) system with the ThCr$_2$Si$_2$-type tetragonal structure (space group: $I4/mmm$, No. 139). The rich variety of electronic properties have been reported such as magnetic ordering, moderate heavy fermion, intermediate valence, and valence transition from more than 15 EuT$_2$X$_2$ compounds and their element substituted systems. For example, in EuFe$_2$Si$_2$ and EuAg$_2$Si$_2$, Eu ions are trivalent and divalent, respectively, [1] and EuPd$_2$Si$_2$ is an intermediate valence compound indicating a significant temperature dependent valence change below 200 K. [2] It is characteristic that the temperature dependence of the electrical resistivity indicates broad maximum at $T^\rho_{\text{max}}$ where the steep valence change occurs. In order to overview the electronic properties of ThCr$_2$Si$_2$-type EuT$_2$X$_2$ compounds, we tentatively plotted the magnetic ordering temperature $T^\text{mag}$ with Eu$^{2+}$ compounds and $T^\rho_{\text{max}}$ of intermediate valence (IV) compounds with respect to the lattice parameter along the c-axis, as shown in Fig. 1.

From a brief look, the compounds with longer c-axis lattice parameter order magnetically, and several compounds with $c \approx 10.1$ Å reveal intermediate valence state. In this plot, EuRh$_2$Si$_2$ and EuNi$_2$Ge$_2$ stands around the boarder between magnetically ordered state (Eu$^{2+}$) and intermediate valence state. Actually, it is reported that EuRh$_2$Si$_2$ and EuNi$_2$Ge$_2$ indicate pressure-induced valence transition at 1 and 2 GPa, respectively. [3, 4] Eu electronic state of EuRh$_2$Si$_2$ is divalent at ambient pressure and orders antiferromagnetically below a Néel temperature $T_N = 23.5$ K. [5] With increasing pressure $P$, the electronic state is changed abruptly at the critical pressure $P_c \approx 1$ GPa, revealing the first order valence transition. [3] Namely, the temperature dependence of the magnetic susceptibility at 1.00 GPa indicates a hysteresis in the cooling and warming processes. The Eu electronic state at 1.00 GPa is nearly divalent, Eu$^{2+\delta}$ ($\delta \ll 1$), at temperatures higher than the characteristic temperature $T_v$ ($\simeq 38$ K), while it becomes nearly trivalent, Eu$^{3-\delta'}$ ($\delta' < 1$) below $T_v$. Here, $T_v$ is called the valence transition temperature.

As for EuNi$_2$Ge$_2$, Eu electronic state is also divalent at ambient pressure and orders
antiferromagnetically below $T_N = 30$ K. [6] The electronic state is changed abruptly at the critical pressure $P_c \approx 2$ GPa, revealing the first-order phase transition. [4, 7, 8] The temperature dependences of the electrical resistivity and thermoelectric power at 2.3 GPa indicate a clear hysteresis in the temperature cooling and warming processes. [8] It is also reported that the antiferromagnetic transition is also observed at 2.3 GPa.

Although it is reported that there are quite a few EuT$_2$X$_2$ compounds exhibiting valence transition under pressure or element substitution, most of works were done using polycrystalline samples. Recently, we have succeeded in growing single crystals of EuRh$_2$Si$_2$ by the Bridgman method and EuNi$_2$Ge$_2$ by the In-flux method. In order to clarify furthermore the valence transition in EuT$_2$X$_2$ system, we have carried out the electrical resistivity experiments under high pressures using single crystal samples.

2. Experimental Procedure
Single crystals of EuRh$_2$Si$_2$ were grown by the Bridgman method. Details for the single crystal growth were described elsewhere. [9] A typical example of the as-grown single crystal of EuRh$_2$Si$_2$ is shown in the inset of Fig. 2. Each single crystals are small in size, less than 1 mm in length, but we obtained a number of such crystals. The brilliant plane corresponds to the tetragonal (001) plane, which is a characteristic shape of ThCr$_2$Si$_2$-type single crystals. While, single crystals of EuNi$_2$Ge$_2$ was grown by the In-flux method. A detailed sample preparation procedure is described elsewhere. [10]

The specific heat was measured by a thermal relaxation method in the temperature range from 2 to 150 K by the physical property measurement system (PPMS, Quantum Design Co. Ltd.). The electrical resistivity was measured by the conventional four-probe AC method in the temperature range from 3 to 300 K at ambient and under high pressures. Pressure was applied by the Bridgman-anvil-type cell using tungsten-carbide WC opposed anvils with Daphne-7373 oil as a pressure transmitting medium. Pressure inside the pressure cell was determined from the superconducting transition of Pb placed next to the sample.

3. Results and Discussion

Figure 2 shows the temperature dependence of the specific heat of EuRh$_2$Si$_2$ single crystal. Inset shows a photograph of a typical single crystal.

Figure 2 shows the temperature dependence of the specific heat $C$ of EuRh$_2$Si$_2$ single crystal. Reflecting the antiferromagnetic ordering at $T_N = 23.4$ K, a sharp $\lambda$-type anomaly is observed, as indicated by an arrow. A broad hump around 7 K in the specific heat curve is due to a Schottky
peak of the $4f$-spins with $S = 7/2$, where the Zeeman splitting of the degenerated spins is realized due to a large magnetic exchange field in the magnetically ordered Eu compound, as described in EuGa$_4$. [11]

The temperature dependences of the electrical resistivity $\rho(T)$ of EuRh$_2$Si$_2$ under pressures up to 2.12 GPa are displayed in Fig. 3(a). Magnified plot in $\rho(T)$ curves for the results obtained $1.1 < P < 1.7$ GPa is shown in Fig. 3(b) for clarity. At 0 and 0.7 GPa, $\rho(T)$ shows a kink at around 25 K reflecting the antiferromagnetic ordering, which is consistent with the data obtained by polycrystalline samples. [3] Further increasing pressure, the $\rho(T)$ curves of single crystal show drastic changes compared to the results obtained by polycrystalline samples. Thus, the present
resistivity data on a single crystal indicate characteristic features accompanied by the valence transition. At 1.14 GPa, \( \rho(T) \) suddenly drops at 58 K with decreasing temperature, on the other hand, \( \rho(T) \) shows spike-like peak at 77 K with increasing temperature. Such prominent and sharp hysteresis behaviors are seen at 1.39 and 1.69 GPa.

Notice that the valence transition in the warming process, namely from the moderate heavy fermion state to the nearly divalent state, possesses a large drop of the electrical resistivity under \( P = 1.39 \) and 1.69 GPa, as shown in Fig. 3(b). Furthermore, with increasing pressure, the transition from the nearly divalent state to the moderate heavy fermion state in the cooling process indicates a sharp and significantly large jump of the resistivity and decreases nearly quadratically with decreasing temperature, as shown in Fig. 3(b) at \( T_v = 126.9 \) K under 1.69 GPa. Note that the \( \rho(T) \) curve at 1.69 GPa resembles that obtained in Eu(Rh
\( \text{0.5} \text{Ir}_0.5 \text{)}_2\text{Si}_2 \). [12]

On the other hand, the \( \rho(T) \) curve at \( P = 2.12 \) GPa is the same between cooling and warming processes, i.e. no hysteresis behavior was observed. A broad resistivity peak at around 190 K under \( P = 2.12 \) GPa is characteristic, which is discussed later. Figure 4 shows the pressure–temperature phase diagram in EuRh
\( \text{2Si}_2 \), where \( T_N \) and \( T_v \) are the Néel temperature and the valence transition temperature, and \( T^\rho_{\text{max}} \) is the temperature showing a peak of the resistivity curve. “AF” means the antiferromagnetic phase and the critical end point “CEP” of the first order valence transition is marked the closed circle (•). Critical pressure \( P_C \), where the antiferromagnetism is suppressed, is below 1 GPa which is consistent with the data obtained on polycrystals. Hysteresis width with respect to the temperature decreases with increasing pressure and varnishes around 2 GPa.

Figure 5 shows the temperature dependence of the specific heat \( C \) of EuNi
\( \text{2Ge}_2 \) single crystal. A \( \lambda \)-type anomaly is observed at the antiferromagnetic ordering temperature \( T_N = 33.5 \) K, as indicated by an arrow. A broad hump due to a Schottky peak of the 4f-spins, which is even more clearer than that of EuRh
\( \text{2Si}_2 \), around 10 K is observed.

![Figure 5. Temperature dependence of the specific heat of EuNi
\( \text{2Ge}_2 \) single crystal. Inset shows a photograph of a typical single crystal.](image)

The temperature dependences of the electrical resistivity \( \rho(T) \) below and above 2 GPa are displayed in Figs. 6(a) and 6(b), respectively. Note that the resistivity is vertically shifted in Fig. 6(b) for clarity. Below 2 GPa, electrical resistivity increases monotonically with increasing pressure. The Néel temperature is also gradually increases with a rate of 6.3 K/GPa. Critical pressure \( P_C \), where the antiferromagnetism varnishes, is about 2.1 GPa in EuNi
\( \text{2Ge}_2 \), which is practically consistent with the previous studies. [4, 7, 8] At 2.17 GPa, \( \rho(T) \) curve shows a clear hysteresis around 60 K, indicating a first order valence transition. \( \rho(T) \) drops with two-steps
Figure 6. Temperature dependences of the electrical resistivities of EuNi$_2$Ge$_2$ for the current along the [100] direction under (a) lower pressure below 1.6 GPa and (b) higher pressure region 2 < P < 3.5 GPa.

Figure 7. Pressure – temperature phase diagram in EuNi$_2$Ge$_2$, where $T_N$ is the Néel temperature, $T_v$ the valence transition temperature, and $T_{\rho \text{max}}$ the temperature showing a peak of the resistivity curve. “AF” means antiferromagnetic phase and the critical end point “CEP” of valence transition is marked as a closed circle (●).

at $T_v$. So far, it is not clear that the two-step decrease corresponds to the two different valence transitions or due to extrinsic reason(s) such as inhomogeneity of sample itself and/or pressure. Nevertheless, it was previously reported that there were two-step decrease of $\rho(T)$ at 2.3 GPa measured on the polycrystalline sample of EuNi$_2$Ge$_2$. [8] Further pressure experiments are in progress in order to clarify the electronic properties around $P_v$ in detail. The $\rho(T)$ anomaly changed spike-like one, above 2.59 GPa and the sharp spike-like $\rho(T)$ becomes broadened for further increasing pressure. As discussed later, $\rho(T)$ at 3.60 GPa shows single broad peak without hysteresis, implying that the electronic state becomes a moderate heavy fermion state.
Figure 8. Temperature dependences of the electrical resistivities in (a) EuRh$_2$Si$_2$ at 2.12 GPa, (b) EuNi$_2$Ge$_2$ at 3.60 GPa, (c) EuPd$_2$Si$_2$, (d) EuIr$_2$Si$_2$, and (e) EuCo$_2$Si$_2$

Figure 7 shows the constructed pressure – temperature phase diagram in EuNi$_2$Ge$_2$ from the present single crystal study. The obtained pressure – temperature phase diagrams on EuRh$_2$Si$_2$ and EuNi$_2$Ge$_2$ are quite identical. Magnetic ordering state with Eu$^{2+}$ is changed to the nearly trivalent state through the first order valence transition, critical end point of the valence transition, and moderate heavy fermion state. The first order valence transition is characterized by a sudden change of electrical resistivity and electrical resistivity indicates a spike-like shape as approaching to the critical end point. Moderate heavy fermion state, characterized by a gradual valence change with respect to the temperature, is accompanied by a broad peak of the resistivity. This pressure – temperature phase diagram can be a universal phase diagram in EuTi$_2$X$_2$ and might be applicable to the other Eu compounds.

It is interesting to compare the present electrical resistivities in the moderate heavy-fermion state in EuRh$_2$Si$_2$ and EuNi$_2$Ge$_2$ with the resistivities of EuPd$_2$Si$_2$, EuIr$_2$Si$_2$, and EuCo$_2$Si$_2$ [13, 12, 14, 15], as shown in Fig. 8. EuPd$_2$Si$_2$ and EuIr$_2$Si$_2$ are well-known valence cross-over compounds. As shown in Fig. 8(c) and 8(d), the valence crossover is observed around $T_{\rho_{\text{max}}}$ = 170 and 150 K in EuPd$_2$Si$_2$ and EuIr$_2$Si$_2$, respectively, as the broad peak in the temperature dependence of the electrical resistivity. [12] From the Mössbauer and photoemission spectroscopic experiments [13, 16, 12], it was clarified that the valence of EuPd$_2$Si$_2$ is 2.22 at room temperature, starts to increase continuously from 200 K, and gradually saturates below 100 K, reaching a value of 2.74 at 20 K. In the case of EuIr$_2$Si$_2$, the Eu valence of 2.3 at 290 K gradually increases and reaches a value of 2.8 at 4.2 K, with a slightly steeper increase around 150 K. [17] On the other hand, Eu valence in EuCo$_2$Si$_2$ is nearly trivalent (Eu$^{3+}$), where the electrical resistivity shows normal metallic behavior. [18] From these results, it can be concluded that the electronic states in EuRh$_2$Si$_2$ at 2.12 GPa and EuNi$_2$Ge$_2$ at 3.60 GPa are a moderate heavy fermion state with gradual change of Eu valence with respect to the temperature. Actually, $\rho(T)$ in EuRh$_2$Si$_2$ shows normal metallic behavior around 5 GPa, which is similar to $\rho(T)$ in EuCo$_2$Si$_2$. [9, 14] It is also expected that the $\rho(T)$ curve in EuNi$_2$Ge$_2$ turns into that of EuCo$_2$Si$_2$.
under higher pressure than 3.60 GPa.

4. Summary
We have succeeded in growing single crystals of EuRh$_2$Si$_2$ and EuNi$_2$Ge$_2$ and studied electronic properties under high pressure. In EuRh$_2$Si$_2$, antiferromagnetism is suppressed below 1 GPa and first order valence transition was observed between 1 and 2 GPa. Critical end point of the first order valence transition is estimated as $P_{CEP} \approx 2.05$ GPa and $T_{CEP} \approx 170$ K. In EuNi$_2$Ge$_2$, antiferromagnetism is suppressed around 2 GPa and first order valence transition was observed between 2.17 and 3.22 GPa. Critical end point in EuNi$_2$Ge$_2$ is estimated as $P_{CEP} \approx 3.5$ GPa and $T_{CEP} \approx 210$ K. Corresponding pressure – temperature ($P$–$T$) phase diagrams of both EuRh$_2$Si$_2$ and EuNi$_2$Ge$_2$ are constructed. The obtained $P$–$T$ phase diagram might be a universal phase diagram of EuT$_2$X$_2$ compounds.

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