

Pressure-Induced Valence Transition in Antiferromagnet EuRh_2Si_2

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Considering the unique properties of EuRh_2Si_2 from the viewpoint of the Eu valence, we have examined its physical properties under external pressure. At ambient pressure, EuRh_2Si_2 is an antiferromagnet with a Néel temperature T_N of 25 K, and the Eu ion is in the divalent state. The application of pressure up to 0.84 GPa slightly shifts T_N toward higher values. Under pressures higher than 1.00 GPa, an abrupt first-order valence transition emerges simultaneously with the disappearance of antiferromagnetism. For $P = 1.17$ GPa, the valence change associated with valence transition is roughly estimated to be ~ 0.19 from the thermal expansion anomaly. The valence transition temperature T_V increases rapidly with increasing pressure. The temperature–pressure phase diagram of EuRh_2Si_2 is very similar to those of the other systems showing pressure-induced valence transition.

KEYWORDS: pressure, europium, antiferromagnetism, valence transition

Recently, valence fluctuation and valence transition have received much attention since they have been found to be associated with non-Fermi liquid behavior and exotic superconductivity.^{1,2)} Valence transition is a change in the number of 4f electrons as a function of temperature, magnetic field, or pressure in rare-earth alloys and compounds. When valence transition occurs, physical properties such as magnetism, volume, and electrical resistivity are affected significantly. Some Eu-based compounds exhibit a relatively large valence variation^{3–5)} compared with Ce- or Yb-based ones.^{6,7)}

The Eu ion can be either divalent (Eu^{2+} , $4f^7$, $J = 7/2$) or trivalent (Eu^{3+} , $4f^6$, $J = 0$) in compounds. The former ion has a large magnetic moment of $7\mu_B$ and a larger volume, while the latter has no magnetic moment and a smaller volume. In some special cases, the Eu valence becomes unstable between Eu^{2+} and Eu^{3+} . Chevalier *et al.* summarized the Eu valence state in EuT_2Si_2 (T = transition metal).⁵⁾ In the case of T = Cu, Pd, and Ir, which are located on a diagonal line in the periodic table, the Eu valence becomes unstable and changes from Eu^{3+} to Eu^{2+} with an increase in temperature. On the right side of the line (T = Ag, Pt, Au), the valence is divalent, whereas on the left side of the line (T = Fe, Co, Ni, Ru, Rh), it is basically trivalent. Interestingly, only in the case of T = Rh, the Eu ion is in the divalent state and exhibits an antiferromagnetic order at $T_N = 25$ K.^{8,9)} With respect to the isomer shift (IS) of the ^{151}Eu Mössbauer effect at room temperature, the IS value of EuRh_2Si_2 relative to the SmF_3 source is -8.3 mm/s,⁵⁾ which shifts somewhat from that of the other divalent compounds (~ -10 mm/s) toward that of the trivalent compounds (~ 0 mm/s). These results suggest that the valence state is in the vicinity of an unstable valence. Taking into consideration the difference in volume between Eu^{2+} and Eu^{3+} , we expected that applying pressure to EuRh_2Si_2 would shift the valence state toward the trivalent direction and induce the Eu valence change, as is observed in compounds with T = Cu, Pd, and Ir. Several pressure-induced shifts in the valence state have already been investigated, and a pressure-induced valence transition was found in $\text{Eu}(\text{Pd}_{0.8}\text{Au}_{0.2})_2\text{Si}_2$,¹⁰⁾ EuNi_2Ge_2 ,^{11,12)} EuPd_2Ge_2 ,¹¹⁾

$\text{EuNi}_2(\text{Ge}_{1-x}\text{Si}_x)_2$ ($x = 0.85\text{--}0.90$),¹³⁾ and EuPt_2Si_2 .¹⁴⁾ The valence transition pressure P_V is relatively high in pure systems, but low in substituted systems. There are also examples of valence transition induced by chemical pressure in $\text{EuNi}_2(\text{Ge}_{1-x}\text{Si}_x)_2$ ($x = 0.70\text{--}0.82$).¹⁵⁾

In the present article, we report that applying a pressure of ~ 1 GPa to EuRh_2Si_2 induces valence transition simultaneously with a sudden collapse of antiferromagnetism. We also examine the low-temperature behavior just above P_V . Since P_V is sufficiently low to be generated using a normal piston–cylinder-type pressure cell, this sample is suitable for examining pressure-induced valence transition by various experimental methods.

A polycrystalline sample of EuRh_2Si_2 was prepared by arc-melting constituent elements under an Ar atmosphere. The purities of the starting metals were higher than 99.9%. The powder X-ray diffraction (XRD) pattern of the sample at room temperature confirms that the sample is in a single phase with a tetragonal ThCr_2Si_2 -type structure. The lattice constants $a = 4.087$ Å and $c = 10.23$ Å, which were determined from the XRD pattern, are in good agreement with those reported in ref. 9. Electrical resistivity and linear thermal expansion under high pressure were measured simultaneously in the temperature range between 2 and 280 K. Only at 1.07 and 1.17 GPa was the measurement of the resistivity carried out down to 250 mK using a cryogenic dilution refrigerator developed by one of the authors.¹⁶⁾ The sample was cut into a rectangular parallelepiped shape ($\sim 2 \times 2 \times 1$ mm³). Four platinum wires for the resistivity measurement and a strain gauge (Kyowa Dengyo KFL-02-120-C1-11) were glued on one side of the sample and on the other side with silver epoxy (EPO-TEK H20S) and adhesive (Kyowa Dengyo PC-6), respectively. The resistivity was taken using an ac resistance bridge (Linear Research LR-700). The linear thermal expansion was observed by the standard two-gauge method.¹⁷⁾ A dummy (reference) gauge was glued on a molybdenum metal (4N). Pressure was generated up to 2 GPa using a piston–cylinder-type pressure cell, which consists of inner (NiCrAl alloy) and outer (CuBe alloy) cylinders. The sample and a tin manometer were placed into a Teflon cell filled with a pressure-transmitting medium consisting of a mixture of two types of Fluorinert in a ratio of FC70 : FC77 = 1 : 1. The Teflon cell was inserted

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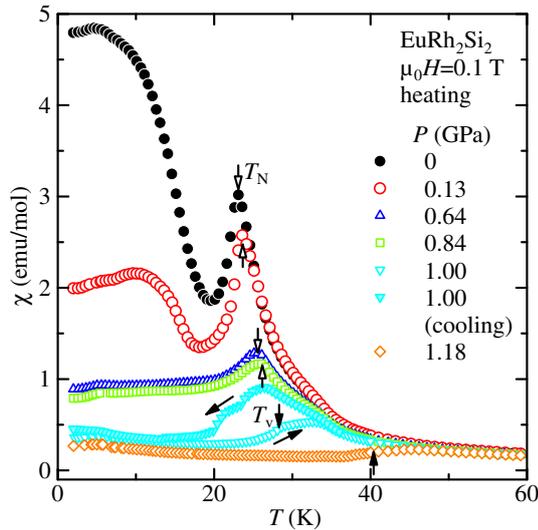


Fig. 1. (Color online) Magnetic susceptibility measured at a magnetic field of 0.1 T during heating as a function of temperature under various pressures. The open and solid arrows denote the Néel temperature T_N and valence transition temperature T_v , respectively. Only for 1.00 GPa was the susceptibility measured during cooling and the thermal hysteresis observed, which implies a first-order transition.

into the pressure cell and pressed by pistons made of nonmagnetic tungsten carbide. Magnetization measurement under high pressure was carried out using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS) in the temperature range between 2 and 300 K. Pressure was applied up to 1.2 GPa using the same type of pressure cell made of nonmagnetic CuTi alloy and pistons made of zirconia to reduce the magnetization signal from the pressure cell. Daphne 7373 was employed as a pressure-transmitting medium. In both measurements, pressure was calibrated from the pressure dependence of the superconducting transition temperature of tin.

Figure 1 shows the temperature dependence of the magnetic susceptibility χ measured at a magnetic field of 0.1 T under various pressures. At ambient pressure, the susceptibility has a sharp peak at $T_N = 23$ K and increases considerably below $T = 19$ K with decreasing temperature. The latter seems to be a ferromagnetic behavior. For this compound, a positive Weiss temperature estimated from the Curie–Weiss behavior at high temperatures has been reported in previous studies.⁹⁾ As reported in ref. 9, the susceptibility measured at a magnetic field of 1 T has no peak at T_N and continues to increase down to 2 K, which indicates that magnetic moments arranged antiferromagnetically in a zero field are easily oriented ferromagnetically by applying a magnetic field of 1 T. This result is in agreement with the notion that this system is on the verge of showing ferromagnetism. With pressure application up to 0.84 GPa, the peak at T_N , which becomes smaller and slightly broader, shifts slightly at higher temperatures. In addition, the susceptibility below $T = 40$ K is depressed markedly. The ferromagnetic increase in χ below 19 K disappears above 0.64 GPa. For $P \geq 1.00$ GPa, the peak becomes much broader and shifts more rapidly at higher temperatures, which is a different behavior from that for $P \leq 0.84$ GPa. For $P = 1.00$ GPa, a large thermal hysteresis is observed, which is indicative of first-order phase transition. In addition, χ at

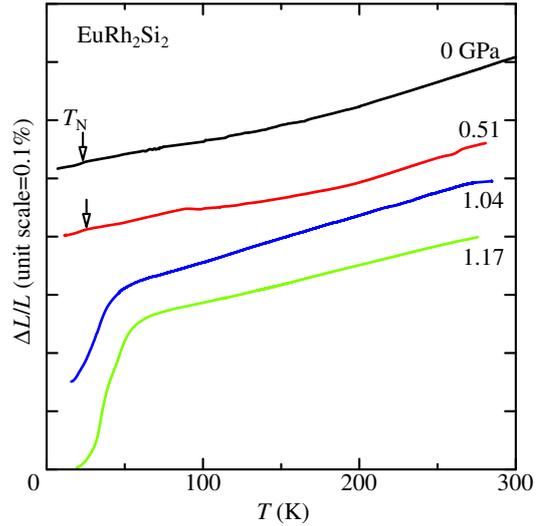


Fig. 2. (Color online) Linear thermal expansion as a function of temperature under various pressures. The open arrows denote the Néel temperature T_N .

the lowest temperature is one order of magnitude smaller than that under ambient pressure. These results suggest that the antiferromagnetic transition at T_N disappears and that first-order valence transition toward a nonmagnetic trivalent state is induced by external pressure. We define the valence transition temperature T_v as the temperature at which $d\chi/dT$ is maximum. For $P = 1.00$ GPa, two-stage valence transition occurs during cooling. It is unknown whether such two-stage valence transition is intrinsic or due to the inhomogeneity of external pressure and/or the sample, but the transition during heating is of the one-stage type. T_v is determined only from the data measured during heating. It was found that the pressure dependence of T_v was much larger than that of T_N . On the other hand, the susceptibility at temperatures higher than 50 K is almost independent of pressure. In these pressure ranges, the Curie–Weiss behavior at high temperatures is preserved.

To ensure the valence transition observed in the susceptibility measurement, the linear thermal expansion $\Delta L/L$ is examined under external pressure, as shown in Fig. 2. Since $\Delta L/L$ was measured using a polycrystalline sample, the volume expansion $\Delta V/V$ is estimated from $3\Delta L/L$. For ambient pressure and $P = 0.51$ GPa, a normal thermal expansion with a volume expansion coefficient of $\sim 2 \times 10^{-5}$ is observed in the temperature range between T_N and room temperature. Below T_N , a small volume contraction accompanied by the antiferromagnetic order is visible, which is similar to that observed in another Eu-based antiferromagnet, EuNi_2Ge_2 .¹⁸⁾ This behavior reminds us that applying pressure stabilizes the antiferromagnetic phase. Actually, we observed a slight increase in T_N with pressure in Fig. 1. For $P = 1.00$ and 1.04 GPa, a normal thermal expansion is observed at higher temperatures, while the volume decreases markedly with decreasing temperature. Since the volume decrease occurs simultaneously with the reduction in the susceptibility, it is confirmed that these phenomena are associated with valence transition toward a nonmagnetic trivalent state with a smaller volume. The $\Delta V/V$ associated with valence transition is estimated to be ~ 0.45 and $\sim 0.80\%$ for 1.04 and 1.17 GPa, respectively.

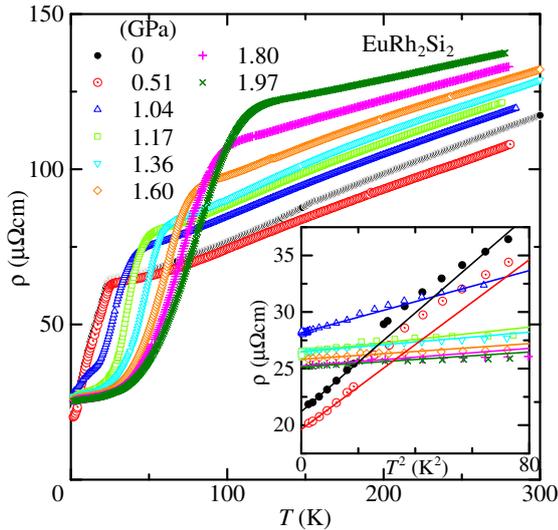


Fig. 3. (Color online) Electrical resistivity as a function of temperature under various pressures. The inset demonstrates the T^2 dependence of the resistivity at the lowest temperature. The solid lines denote the results obtained by fitting $\rho(T) = \rho_0 + AT^2$ to the resistivity data.

Compared with that of $\text{EuNi}_2(\text{Si}_{0.25}\text{Ge}_{0.75})_2$,¹⁸⁾ the magnitude of the volume anomaly is smaller, which would be due to the smaller valence change. Felner and Nowik reported the lattice parameters of and magnetism in RRh_2Si_2 ($R = \text{rare earth}$) systems.⁸⁾ In these systems, only Eu is exceptionally divalent, while the others are trivalent. Considering the lanthanoid contraction in the RRh_2Si_2 system, we estimated the lattice volume of the hypothetical $\text{Eu}^{3+}\text{Rh}_2\text{Si}_2$ and found it to be $V = 163.8 \text{ \AA}^3$. Assuming that the Eu ion is divalent in the present sample with a lattice volume of 170.9 \AA^3 , the volume change associated with a valence change from $2+$ to $3+$ is determined to be $\Delta V/V \sim 4.1\%$. This means that the observed $\Delta V/V$ of $\sim 0.80\%$ at 1.17 GPa corresponds to a Eu valence change Δv of 0.19.

Figure 3 demonstrates the temperature dependence of the electrical resistivity ρ measured during heating under various pressures. A magnified graph in the low-temperature range is shown in Fig. 4. For ambient pressure, the ρ - T curve, which generally shows a metallic behavior, exhibits a steep bend at T_N and a linear temperature dependence above 100 K. The curve is similar to those of other Eu-based antiferromagnets with the ThCr_2Si_2 -type structure.^{12,13,18–20)} Below T_N , the resistivity decreases more rapidly, which reflects the suppression of conduction-electron scattering by paramagnetic local moments of Eu^{2+} . The application of a pressure of 0.51 GPa does not markedly change the shape of the curve but slightly shifts T_N toward higher values, which is consistent with the present result of the susceptibility measurement. For $P = 1.04$ GPa, the steep bend is abruptly transferred into a broad one and the temperature dependence of ρ below $T = 40$ K is completely changed, which is suggestive of the collapse of antiferromagnetism and the occurrence of valence transition. In the case of $\text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2$,^{12,18)} a valence transition is observed as a peak in the ρ - T curve. Assuming that the lifetime of a conduction electron is shorter than the valence fluctuation time, we considered that the peak might have arisen from the most disordered potential caused by the random arrangement of Eu^{2+} and Eu^{3+} ions when the valence goes through $v = 2.5$.

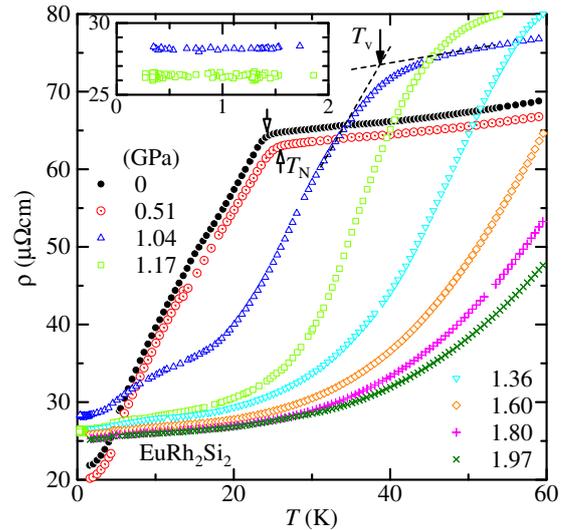


Fig. 4. (Color online) Magnified graph in the low-temperature region of the resistivity as a function of temperature under various pressures. The inset indicates the resistivity data in the temperature range from 0.25 to 2 K at $P = 1.04$ and 1.17 GPa.

In the present case, no such behavior was observed. The valence variation Δv associated with valence transition was estimated to be ~ 0.19 for 1.17 GPa from the thermal expansion, which suggests that the mean Eu valence does not pass through $v = 2.5$. Consequently, the potential is not as disordered as that in $\text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2$, and the scattering by phonons dominates the temperature dependence of ρ . Therefore, no peak is found in the present ρ - T curve. We define the valence transition temperature T_v as the point of intersection of two lines extrapolated from the ρ - T curve below and above the temperatures of the broad bend, as shown in Fig. 4. With the application of a higher pressure, the broad bend, namely, the valence transition temperature T_v , moves rapidly toward higher values, and the ρ - T curves at the lowest temperatures become concave up. dT_v/dP is determined to be $\sim 74 \text{ K/GPa}$, which is smaller than that of $\text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2$, $\sim 105 \text{ K/GPa}$.¹³⁾ Using the Clausius–Clapeyron relation, we evaluate the entropy change associated with valence transition as $\Delta S = 5.2 \text{ J/(mol K)}$, which is much smaller than $R \ln(2J + 1) = 17.3 \text{ J/(K mol)}$ expected for the paramagnetic local moments of Eu^{2+} ($J = 7/2$). This result, which is in contrast to that of $\text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2$,¹³⁾ implies the difference in the characteristics of valence transition between EuRh_2Si_2 and $\text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2$. However, the reason for this remains unknown and further studies are necessary. The ρ - T curve for $P = 1.04$ GPa is similar in shape to that for $P \leq 0.51$ GPa below $T = 20$ K and that for $P = 1.17$ GPa above $T = 20$ K, which means that the pressure of 1.04 GPa is close to the boundary between antiferromagnetic order and valence transition. The inset of Fig. 3 shows the ρ - T^2 curves at the lowest temperatures. The residual resistivity is largest at $P = 1.04$ GPa, but its enhancement factor is ~ 1.3 at most. For all the pressures studied, the T^2 dependence of ρ with its coefficient A of 0.016 – $0.2 \mu\Omega \text{ cm/K}^2$ is observed at the lowest temperatures, which indicates a Fermi-liquid behavior. Since this system exhibits discontinuous valence transition, it is difficult to tune the Eu valence to a quantum critical point. The inset of Fig. 4 shows the resistivity data in

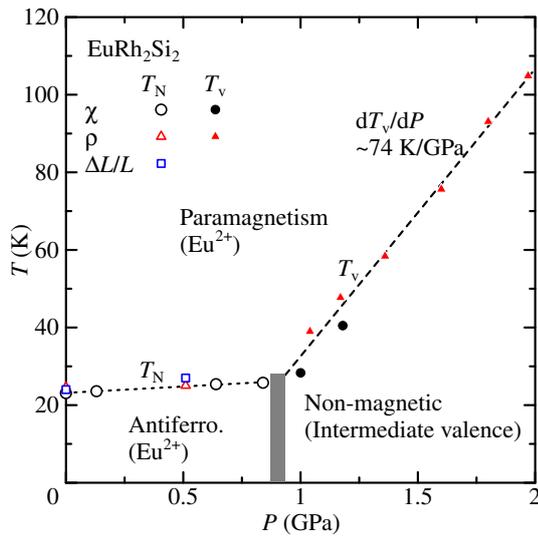


Fig. 5. (Color online) Temperature vs pressure phase diagram in EuRh_2Si_2 . The open and solid symbols denote the Néel temperature T_N and the valence transition temperature T_v determined from the present measurements, respectively.

the temperature range from 0.25 to 2 K for $P = 1.04$ and 1.17 GPa, where antiferromagnetism just collapsed. The resistivity is almost independent of temperature down to 0.25 K and exhibits no superconducting behavior. These results suggest that no quantum critical behavior is found.

Figure 5 shows a T - P phase diagram of EuRh_2Si_2 determined from the present measurements. There are three features in the phase diagram. (i) The Néel temperature T_N is almost independent of or enhanced slightly with pressure. Although the application of pressure destabilizes the Eu^{2+} ion, it stabilizes the antiferromagnetic phase of Eu^{2+} . (ii) The antiferromagnetic phase disappears abruptly, and simultaneously a nonmagnetic (possibly intermediate valence) phase emerges. (iii) After the collapse of antiferromagnetism, in contrast, the valence transition temperature T_v increases significantly with pressure. These are very similar to the behaviors of $\text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2$ ($x = 0.85-1$)^{12,13} and YbInCu_4 ²¹⁻²³ under external pressure. Both systems are associated with the competition between valence transition and magnetic order. In addition, if pressure is replaced with the amount of element substituted in the phase diagram, the P - T phase diagram becomes analogous to the temperature-substitution phase diagrams of $\text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2$ ¹⁵ and $\text{Eu}(\text{Pd}_{1-x}\text{Au}_x)_2\text{Si}_2$.²⁴ Such phase diagrams might be universally characteristic of a system showing valence transition.

In conclusion, we observed an anomalous behavior of antiferromagnetic EuRh_2Si_2 and examined its physical properties under external pressures. The application of pressure first increases the Néel temperature T_N slightly and then causes the sudden collapse of antiferromagnetism simultaneously with the occurrence of first-order valence transition at $P \sim 1$ GPa. The valence transition temperature T_v increases significantly with increasing pressure. This behavior is analogous to those observed in other Eu- and Yb-based systems associated with the competition between magnetic order and valence transition. The valence variation associated with valence transition is estimated from the thermal expansion to be $\Delta v \sim 0.19$, which is slightly smaller than those in the other Eu-based systems. Since

the pressure necessary to induce the valence transition is sufficiently low to be generated using a piston-cylinder-type pressure cell, further detailed investigations of valence transition are needed. Quite recently, Seiro and Geibel have reported the $\text{Eu}(\text{Rh}_{1-x}\text{Ir}_x)_2\text{Si}_2$ system as a new valence-fluctuating system.²⁵ The substitution of Ir for Rh, which decreases lattice parameters, causes the collapse of antiferromagnetism and induces first-order transition simultaneously. Since Ir is in the same row as Rh in the periodic table, Ir substitution may correspond to an external pressure in the present study. It would be fruitful to compare the two studies to understand valence transition.

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