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Pressure and magnetic field effects on the valence transition of $EuRh_2Si_2$

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ABSTRACT

We have measured the X-ray absorption spectra (XAS), electrical resistivity and magnetic susceptibility of $EuRh_2Si_2$, which undergoes a valence transition under high pressures. A sharp decrease in the Eu valence determined from the XAS was observed at around 70 K in the temperature dependence at P = 1.2–1.9 GPa. In the temperature dependence of electrical resistivity and magnetic susceptibility, we observed jumps associated with the temperature-induced valence transition under high pressures. The magnetoresistance detected a field-induced valence transition. The results are discussed from the thermodynamic point of view.

1. Introduction

Valence instability of 4f electron systems has been extensively studied for over a half century. Some of the rare-earth compounds with Ce, Sm, Eu and Yb are known to show intermediate valence or valence fluctuations due to the 4f level located near the Fermi level. Among them, Eu compounds exhibit strong temperature or pressure dependence of the mean valence. First example of such behavior was $EuPd_2Si_2$ reported by Sampathkumaran et al. [1]. This compound undergoes a precipitous, but continuous valence change at around 150 K. Segre et al. found that the substitution of Au for Pd causes an abrupt change in the valence in its temperature dependence [2]. A similar temperature-induced valence transition was also observed in $Eu(Pd_{1-x}Pt_x)_2Si_2$ [3]. Another typical example is $EuNi_2Ge_2$, in which a valence transition was first observed in the pressure dependence at room temperature [4]. Hesse et al. observed a temperature-induced valence transition at around 80 K under a pressure of 1.9 GPa [5]. In 2010s, two Eu compounds were reported to undergo a valence transition. Seiro and Geibel observed the temperature-induced valence transition in $Eu(Rh_{1-x}Ir_x)_2Si_2$ single crystals with $0.35 \le x \le 0.5$ [6]. Our group found that $EuRh_2Si_2$ undergoes a sharp valence transition under high pressures of $P > 1.0$ GPa [7]. This compound is antiferromagnetic below the Néel temperature of 25 K at ambient pressure [8]. Compared with the other Eu-based valence transition systems, the valence transition temperature, T_V, of $EuRh_2Si_2$ is substantially low, being as low as 35 K at P = 1.05 GPa. This means that the energy difference between the divalent and trivalent states is small. Therefore, the valence transition is expected to be sensitive to external pressure and magnetic field. Actually, we observed a field-induced valence transition at a moderate valence transition field, B_V, below 10 T [9]. In order to study the nature of valence transition of $EuRh_2Si_2$, we have measured X-ray absorption spectra, electrical resistivity and magnetic susceptibility under high pressures.

2. Experimental details

Polycrystalline $EuRh_2Si_2$ samples were prepared by arc-melting under argon atmosphere. The purities of the ingredients are 3 N for Eu and Rh, and 5 N for Si. Because of high vapor pressures of Eu, we first synthesized RhSi equiatomic alloys and then melt them together with Eu metals for several times. Excess Eu was added to compensate the weight loss during melting. We confirmed the weight loss of the samples less than 3 wt%. The samples wrapped in Ta foil were sealed in an evacuated quartz tube and they were annealed at 900 °C for five days. The X-ray diffraction pattern has shown that the samples have a single phase with the tetragonal $ThCr_2Si_2$-type structure.

X-ray absorption spectra (XAS) at the Eu L_3-edge were measured at ambient pressure and under high pressures using the beam lines BL01B1 and BL39XU of SPring-8, respectively. The measurements under high pressures were carried out in a diamond anvil cell (DAC). We used nano-polycrystalline diamond (NPD) anvils to remove Bragg diffraction from the anvils, which frequently appears near the Eu L_3-edge [10,11]. The methanol-ethanol mixtures with a ratio of 4:1 were used as a pressure-transmitting medium. The pressure was calibrated

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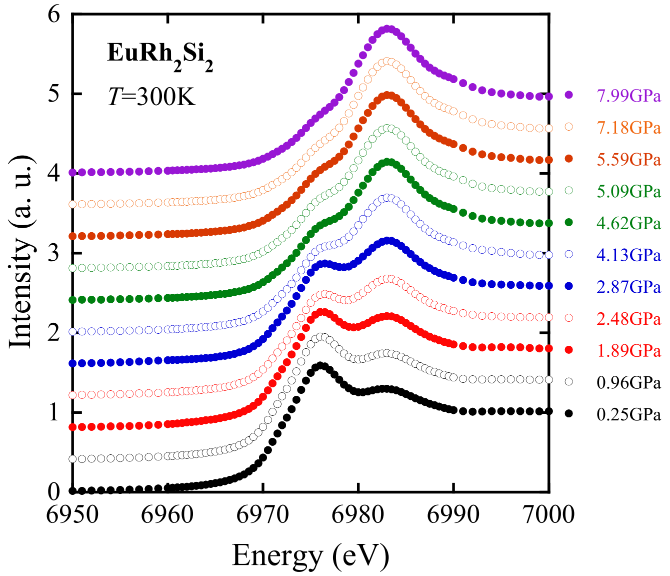

Fig. 1. X-ray absorption spectra (XAS) of EuRh$_2$Si$_2$ at the Eu L_3-edge under various pressures at room temperature.

using the fluorescence from ruby, which was mounted with the sample in the DAC.

Electrical resistivity measurements were carried out by a standard four-probe technique using an a.c. resistance bridge between 4.2 K and 60 K at P =1.1 GPa. The magnetic field, B, was applied parallel to the electric current. Magnetic susceptibility was measured in a commercial SQUID magnetometer between 4.2 K and 130 K at P =1.9 GPa. NiCrAl and CuBe clamp cells were used to generate a pressure for resistivity and susceptibility measurements, respectively. Daphne 7373 was employed as a pressure-transmitting medium for these measurements.

3. Experimental results

Fig. 1 shows the XAS of EuRh$_2$Si$_2$ at room temperature up to 8 GPa. Two peaks are visible in each spectrum, one is centred at around 6976 eV with the 2p^{5}4f^7 final state and the other at around 6983 eV with the 2p^{5}4f^6 final state. At low pressures, the divalent peak is dominant. With increasing pressure, the trivalent peak evolves and it becomes pronounced at the highest pressure of 8 GPa. The results were analyzed in a standard procedure. The spectrum was decomposed into two subspectra, each of them consisting of an arctangent and a Lorentzian. The Eu valence, ν, was determined from the intensity ratio of the two subspectra. The pressure dependence of ν of EuRh$_2$Si$_2$ at room temperature is illustrated in Fig. 2(a). It is found that the Eu valence is strongly dependent on pressure. EuRh$_2$Si$_2$ is close to a divalent state at P = 0.25 GPa, while it is nearly trivalent at P = 8 GPa. We have measured XAS of EuRh$_2$Si$_2$ at various temperatures under high pressures. Fig. 2(b) displays the temperature dependence of ν measured at ambient pressure, 1.2–1.9 GPa and 3.9–4.5 GPa. At each measurement, the applied pressure was calibrated. We found the pressure slightly temperature dependent. At ambient pressure, ν is about 2.2 and it is independent of temperature. The observed ν value is slightly larger than two. There are two possible reasons for this discrepancy. One is the difficulty of precise determination of ν by XAS for Eu compounds due to the final state effects [12,13]. It has been reported that some divalent or trivalent Eu compounds have double peaks in XAS. Therefore, the ν value of the divalent compounds is often overestimated. The other is the case that EuRh$_2$Si$_2$ is not purely divalent. The saturation magnetization of EuRh$_2$Si$_2$ in high magnetic fields is 5–5.5 μ_B/Eu at low temperatures [8,14], which is definitely smaller than the theoretical value of Eu^{2+}, 7 μ_B. This fact may suggest that EuRh$_2$Si$_2$ is in an intermediate valence state close to Eu^{2+} at ambient pressure. To clarify this point, further experiments are necessary. Anyway, the XAS of EuRh$_2$Si$_2$ indicate that the nearly divalent state is stable in the whole temperature range studied at P = 0 GPa. On the other hand, a sharp decrease in ν was observed at around 70 K at P = 1.2–1.9 GPa. This is the direct evidence of a temperature-induced valence transition in EuRh$_2$Si$_2$ under high pressures. At P = 3.9–4.5 GPa. ν shows rather weak temperature dependence and it decreases from 2.87 to 2.61 with increasing temperature from 3 K to 300 K.

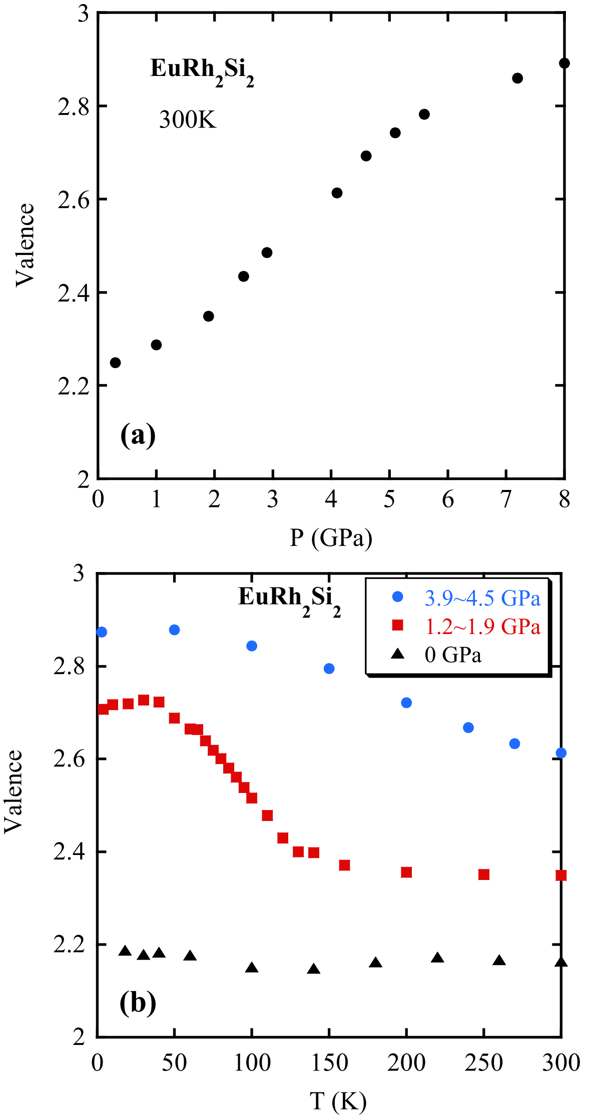

Fig. 2. (a) The Eu valence of EuRh$_2$Si$_2$ at room temperature determined from the XAS as a function of pressure. (b) Temperature dependence of the Eu valence of EuRh$_2$Si$_2$ at various pressures.

Fig. 3 shows the electrical resistivity, ρ, of EuRh$_2$Si$_2$ as a function of temperature in various magnetic fields up to 12 T at P = 1.1 GPa. The measurements were carried out in the following procedure. After a magnetic field is applied at 4.2 K, the $\rho - T$ curves were recorded with the temperature sequence of 4.2 K → 60 K → 4.2 K. Then, the magnetic field was removed at 4.2 K before the next measurement. In zero field, the resistivity shows clear jumps at T_V on heating, T_V^{up} = 38.5 K and that on cooling, T_V^{down} = 28.4 K. The valence transition is accompanied by a large thermal hysteresis, indicating a first-order phase transition. Higher resistivity above T_V originates from spin disorder scattering due to the onset of Eu^{2+} moments. With increasing B, T_V^{up} decreases slightly up to 7 T, while T_V^{down} is drastically lowered. No valence transition was detected down to 4.2 K on cooling for B ≥ 7 T. The