Effect of pressure on thermopower of EuNi$_2$Ge$_2$

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Abstract. EuNi$_2$Ge$_2$ is antiferromagnetic below $T_N \approx 30$ K with an effective moment $\mu_{\text{eff}} \approx 7.7 \mu_B$, indicating the 4f electron configuration (Eu$^{2+}$) in the ground state. In order to investigate the electronic state of EuNi$_2$Ge$_2$, we have simultaneously measured thermopower $S$ and electrical resistivity $\rho$ at the temperature range between 2 K and 300 K and under pressures up to 3.5 GPa. In the pressure region of $P \lesssim 2.3$ GPa, $\rho$ increases with increasing temperature, and shows an anomaly in the form of a kink at the Néel temperature $T_N$. $S(T)$ also reveals a kink at $T_N$. Both $\rho(T)$ and $S(T)$ indicate a small pressure dependence at the low pressure range. However, $\rho(T)$ and $S(T)$ curves in the low temperature region suddenly change their features at $P \approx 2.3$ GPa, where the magnetic ordering disappears. $\rho$ linearly decreases with decreasing temperature, and shows a sudden drop at the valence transition temperature $T_v \approx 30$ K. $S(T)$ reveals a drastic increase at $T_v$, changing its sign from negative to positive around 35 K, and takes maximum at $T \approx 7$ K. The thermal hysteresis was clearly observed in both $\rho(T)$ and $S(T)$ curves around $T_v$.

1. Introduction

Many Europium-base intermetallic compounds of the RT$_2$X$_2$ family, where R is a rare earth, T is a transition metal and X is silicon or germanium, with tetragonal ThCr$_2$Si$_2$ structure exhibit a change in valence as function of temperature, atomic substitution, pressure and magnetic field from a divalent to a trivalent state. In this series, EuNi$_2$Ge$_2$ is antiferromagnetic below $T_N \approx 30$ K with an effective moment $\mu_{\text{eff}} \approx 7.7 \mu_B$, indicating the 4f electron configuration (Eu$^{2+}$) in the ground state [1]. On the other hand, EuNi$_2$Si$_2$, where Eu is trivalent with the 4f$^7$ electron configuration, indicates a temperature independent magnetic susceptibility [2].

It is well known that the valence of EuNi$_2$(Ge$_{1-x}$Si$_x$)$_2$ changes strongly with temperature, Si concentration, pressure, and magnetic field [2, 3, 4, 5, 6]. The application of external pressure results in the destabilization of the Eu$^{2+}$ state and shifts the divalent state to the trivalent state. Hesse et al. reported the pressure-induced first-order valence transition of EuNi$_2$Ge$_2$ at $T \approx 100$ K under $P \approx 2$ GPa [4]. From the results of pressure and Si doping dependent electrical resistivity $\rho$ of EuNi$_2$(Ge$_{1-x}$Si$_x$)$_2$ with $x \leq 0.15$, it was concluded that the application of pressure and replacement Ge by Si have equivalent effects on the valence transition of EuNi$_2$Ge$_2$ [6].

The intermediate valence state is connected with the hybridization between the localized 4f states and 5d conduction band, resulting high density of states at the Fermi level [7]. Since the electron scattering is sensitive to the electronic state in the vicinity of the Fermi level,
the measurements of the transport properties such as thermopower $S$ and electrical resistivity $\rho$ are instructive in investigating the valence change of the EuNi$_2$(Ge$_{1-x}$Si$_x$)$_2$ system. The measurements of $\rho$ for EuNi$_2$(Ge$_{1-x}$Si$_x$)$_2$ and for other compounds with intermediate valence have been extensively performed under high pressures and in magnetic fields [5, 6, 8, 9, 10]. However, few studies on the thermopower $S$, as far as we know, have been reported in the literature [8, 11]. In this paper, we present experimental results on thermopower $S$ and electrical resistivity $\rho$ of EuNi$_2$Ge$_2$ compound measured under pressures up to 3.5 GPa at temperatures from 2 K to 300 K.

2. Measurement procedures
Polycrystalline sample of EuNi$_2$Ge$_2$ was prepared from pure components by melting in an arc furnace under a protective Ar atmosphere and was subsequently annealed in vacuum at 1100 K for about one week. The ThCr$_2$Si$_2$-type tetragonal structure with lattice parameters of $a = 4.134$ Å and $c = 10.080$ Å was verified by the powder x-ray diffraction (XRD) measurement. No foreign phase was not detected in the XRD profile. The size of sample used for measurements of the electrical resistivity $\rho$ and thermopower $S$ was about $0.5 \times 1 \times 2.5$ mm$^3$.

The measurements of $\rho$ and $S$ were carried out by using the standard four-probe dc method and the differential method with a modified “seesaw heating” procedure [12], respectively. Chromel-constantan thermocouples were used for thermopower measurement. The electrical resistivity $\rho$ and thermopower $S$ were measured simultaneously at temperatures from 2 K to 300 K under pressures up to 3.5 GPa. Hydrostatic pressure was generated using a CuBe-NiCrAl hybrid clamp-type piston cylinder pressure cell with Daphne oil 7373 as the pressure-transmitting medium [13].

3. Results and Discussion
Figure 1 and 2 show the temperature dependence of $\rho$ and $S$ of EuNi$_2$Ge$_2$ at temperatures from 2 K to 300 K under several pressures up to 3.5 GPa, respectively. In the pressure region of $P \lesssim 2.3$ GPa, $\rho$ increases with increasing temperature, and shows an anomaly in the form of a
kink at the Néel temperature $T_N$. The temperature dependence of $S$ also reveals a kink at $T_N$. In the temperature range above $T_N$, the absolute value of $S$ increases with increasing pressure, both $\rho(T)$ and $S(T)$ indicate monotonous temperature dependence in the entire measurement pressure. On the other hand, as shown in Figs. 1 and 2, $\rho(T)$ and $S(T)$ curves in the low temperature region suddenly changes the features at $P = 2.3$ GPa. Figure 3 depicts the enlarged portion of the temperature dependence of $\rho$ and $S$ of EuNi$_2$Ge$_2$ under pressure of $P = 2.3$ GPa in the low temperature range during cooling and warming processes. With decreasing temperature, $\rho$ linearly decreases, having a kink at $T_N \approx 42$ K and a sudden drop at the valence transition temperature $T_V \approx 35$ K. The temperature dependence of $S$ also shows an anomaly at $T_N$ and reveals a drastic increase at $T_V$. As further decreasing temperature, $S$ changes its sign from negative to positive around 35 K, and takes maximum at $T \approx 7$ K. The thermal hysteresis was clearly observed in both $\rho(T)$ and $S(T)$ curves around $T_V$ below $T_N$. In the previous studies, it was reported that the first-order valence transition was observed above the critical pressure $P_c$, where the valence transition appears [6]. The results of $\rho$ and $S$, shown in Fig. 3, indicate that the valence transition takes place at $T_V$ below the Néel temperature $T_N$ under pressure of $P = 2.3$ GPa, suggesting the competition between the magnetically ordered state and the intermediate valence state in EuNi$_2$Ge$_2$. Above the critical pressure $P_c \approx 2.3$ GPa, the magnetic phase transition vanishes, and only the valence transition with thermal hysteresis is observed in both $\rho(T)$ and $S(T)$ curves.

The Néel temperature $T_N$ and the valence transition temperature $T_V$ obtained from the results of $\rho(T)$ are shown in Fig. 4 as function of the external pressure $P$. In the pressure range of $P < P_c$, the pressure dependence of $T_N$, $dT_N/dP \approx 5$ K/GPa, and the temperature behavior of $\rho$ are in good agreement with the results of previous works [6]. At pressures $P > P_c$, the maximum of $\rho$ around the valence transition temperature $T_V$ [10], which is claimed as the indication of the valence transition for the Eu based compounds such as the EuNi$_2$(Ge$_{1-x}$Si$_x$)$_2$ and

![Figure 3. Temperature dependence of $S$ and $\rho$ of the EuNi$_2$Ge$_2$, measured at $P = 2.3$ GPa during cooling and warming processes. The thermal hysteresis was clearly observed in both $\rho(T)$ and $S(T)$ curves below $T_N$, indicated by the empty arrows.](image1)

![Figure 4. Pressure dependence of the magnetic transition temperature $T_N$ and the valence transition temperature $T_V$ of EuNi$_2$Ge$_2$. $T_N$ and $T_V$ were observed at the pressure of $P = 2.3$ GPa. The dotted line indicates the critical pressure $P_c \approx 2.3$ GPa.](image2)
EuCu$_2$(Ge$_{1-x}$Si$_x$)$_2$ systems [6, 5, 14], was not observed in the present work, as shown in Fig. 1. Also, the value of $dT_v/dP \approx 60$ K/GPa is different from the value of $dT_v/dP \approx 100$ K/GPa, reported in literatures [6, 10]. These differences are presumably due to the sample quality or the thermal treatment procedures.

It should be noted that there are differences between the effects of the atomic substitution and of the external pressure on the transport properties of EuNi$_2$Ge$_2$. The thermopower of EuNi$_2$(Ge$_{1-x}$Si$_x$)$_2$ reported in Ref. [11] shows a gradual anomaly around the valence transition temperature $T_v$ without thermal hysteresis, which could be attributed to the coexistence of the high- and the low-temperature phases in the wide temperature range [5]. In contrast, the sample used for the present measurements indicates the sharp valence transition with a distinct thermal hysteresis around $T_v$ in both $S(T)$ and $\rho(T)$ curves under the entire measurement pressure range above $P_c$. As can be seen in Fig. 2, the characteristic feature of $S(T)$ under $P > P_c$ in the low temperature range $T < T_v$ is enhanced by the application of pressure. The temperature dependence of $S$ in the high temperature phase, however, shows approximate pressure independent behavior. The temperature gradient of thermopower $S/T$ at the lowest temperature, which is considerably connected with the electronic state in the vicinity of the Fermi level [15], increases with increasing pressure. This result implies that the development of the low temperature peak of $S(T)$ at $T \approx 7$ K due to application of pressure is related to the increase of hybridization between Eu$^{3+}$- 4f electron and conduction electrons, resulting high electronic density of states at the Fermi level.

In summary, the electrical resistivity $\rho$ and thermopower $S$ of EuNi$_2$Ge$_2$ compound were measured at temperatures from 2 K to 300 K under pressures up to 3.5 GPa. The valence transition from Eu$^{2+}$ to Eu$^{3+}$ with thermal hysteresis was observed at $T_v \approx 35$ K below the Néel temperature $T_N \approx 40$ K under pressure of $P = 2.3$ GPa, indicating the competition between the magnetically ordered state and the intermediate valence state in EuNi$_2$Ge$_2$. The temperature variations of thermopower of EuNi$_2$Ge$_2$ at $T < T_v$ indicate that the application of pressure induce a large modification of the electronic state around the Fermi level.

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