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Pressure Effect on Transport Properties of $EuNi(Si_{1-x}Ge_x)_3$ Compounds

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Abstract

The compounds of $EuNi(Si_{1-x}Ge_x)_3$ order antiferromagnetically. At the temperature T_C below the Néel temperature T_N, $EuNiSi_3$ ($x = 0$) shows an additional magnetic transition into ferromagnetic state. T_N decreases monotonously with increasing the Ge composition x. The Curie temperature T_C decreases rapidly with increasing x and vanishes at the critical composition $x \approx 0.3$. We have measured the electrical resistivity and thermopower of $EuNi(Si_{0.8}Ge_{0.2})_3$, which is a compound near to the boundary between the ferromagnetic and antiferromagnetic ground states in the phase diagram for $EuNi(Si_{1-x}Ge_x)_3$ system, under pressures up to 1.8 GPa at temperatures from 2 to 300 K. The anomalies in $\rho(T)$ and $S(T)$ curves of $EuNi(Si_{0.8}Ge_{0.2})_3$ are observed at $T_C = 16$ K and $T_N = 34$ K at ambient pressure. Both T_C and T_N increase linearly with increasing pressure. The temperature variations of ρ and S of $EuNi(Si_{0.8}Ge_{0.2})_3$ at $P = 1.8$ GPa are almost the same as those of $EuNi(Si_{0.9}Ge_{0.1})_3$ (x=0.1) at ambient pressure, revealing that the effect of pressure on T_N and T_C is the same as that of the increase of Si concentration. The pressure and atomic composition dependences of the magnetic transition temperatures T_N and T_C can be expressed by using the Grüneisen parameters. These results indicate that the changes of T_N and T_C are attributed to the change of atomic volume induced by the applying pressure or the atomic substitution.

Keywords: Electrical resistivity, Thermopower, Pressure effect, Magnetic phase transition

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1 Introduction

In Eu compounds, it is well known to exhibit the valence instability, depending on the temperature, magnetic field, pressure and atomic composition. The accumulated data show that the stable states of Eu^{2+} ($4f^7 6s^2$), Eu^{3+}($4f^6 5d^1 6s^2$) and dynamic intermediate valence state are possible for Eu. The electronic state of Eu^{2+} is magnetic with $J = 7/2$ ($S = 7/2,\ L = 0$), which is the same as that of the corresponding Gd compound, while the Eu^{3+} state is non-magnetic with $J = 0$ ($S = L = 3$). Here, J is a total angular momentum, S is a spin angular momentum, and L is an orbital angular momentum.

In RT_2X_2 with the $ThCr_2Si_2$-type tetragonal structure, for example, $EuNi_2Ge_2$, in which the Eu atoms are in the Eu^{2+} state, manifests an antiferromagnetic order at the $T_N \approx 30$ K. $EuNi_2Si_2$, in which Eu atoms are in the Eu^{3+} state, is the Pauli-paramagnetism with temperature-independent magnetic susceptibility. Interestingly, $EuNi_2Ge_2$ shows the valence transition from divalent- into trivalent-electronic states by the replacement of Ge by Si. Due to a large difference in atomic size between Eu^{2+} and Eu^{3+} ions, the Eu valence depends strongly on the change of the atomic volume induced by the atomic replacement or the applying pressure [1, 2, 3]. On the other hand, RTX_3 (R=rare earth, T=transition metal, and X=Si, Ge) compounds, which crystallize in the $ThCr_2Si_2$-type or $BaNiSi_3$-type tetragonal structures [4], have been studied extensively from the scientific and practical view points. However, few studies on $EuNiX_3$ (X=Si, Ge), as far as we know, have been reported in the literature. In our previous work [5, 6], for the EuNi($Si_{1-x}Ge_x$)$_3$ compounds, we obtained the effective magnetic moment of $\mu_{\rm eff} \approx 7.7\ \mu_B$, which is close to a divalent Eu value of $\mu_{\rm eff} = 7.94\ \mu_B$. The Néel temperature T_N decreases monotonously with increasing the Ge composition x from $T_N = 49$ K for $EuNiSi_3$ to $T_N = 14$ K for $EuNiGe_3$. The Curie temperature $T_C = 16$ K below T_N in $EuNiSi_3$ decreases rapidly with increasing x and vanishes at the critical Ge composition $x \approx 0.3$. At the low temperatures below T_N, the anomalies corresponding to additional magnetic phase transition into another antiferromagnetic state for $x > 0.3$ was observed [7].

In order to investigate the effect of pressure on the magnetic and transport properties of EuNi($Si_{1-x}Ge_x$)$_3$ system, we have performed the measurements of the electrical resistivity ρ and thermopower S of EuNi($Si_{0.8}Ge_{0.2}$)$_3$, which is a compound near to the boundary between the ferromagnetic and antiferromagnetic ground states in the phase diagram for EuNi($Si_{1-x}Ge_x$)$_3$ system, under pressures up to 1.8 GPa at temperatures from 2 to 300 K.

2 Experimental procedures

The polycrystalline samples of EuNi($Si_{1-x}Ge_x$)$_3$ compounds were prepared from the pure components of 3N(99.9 % pure)-Eu, 5N-Ni and 5N-Si(Ge) by melting in an arc-furnace under a protective Ar atmosphere and was subsequently annealed in vacuum at 800 °C for five days. It was reported that $EuNiSi_3$ is $ThCr_2Si_2$-type tetragonal structure with lattice parameters of $a = 4.158$ Å and $c = 9.636$ Å [4], and $EuNiGe_3$ is $BaNiSn_3$-type tetragonal structure with lattice parameters of $a = 4.339$ Å and $c = 9.887$ Å [6]. The tetragonal crystal structure have been confirmed for all compounds of EuNi($Si_{1-x}Ge_x$)$_3$ by the powder X-ray diffraction measurement.

The electrical resistivity ρ was measured by means of the standard four-probe dc method. The differential method with the seesaw-heating procedure was used for the thermopower S measurement [8]. The electrical resistivity and thermopower were measured simultaneously in the temperature range from 2 to 300 K. A clamp-type hybrid piston-cylinder-pressure-cell with Daphne oil 7373 as the pressure transmitting medium was utilized for the measurements of ρ and S under pressures up to 1.8 GPa at the temperatures from 2 to 300 K [9]. In these pressure

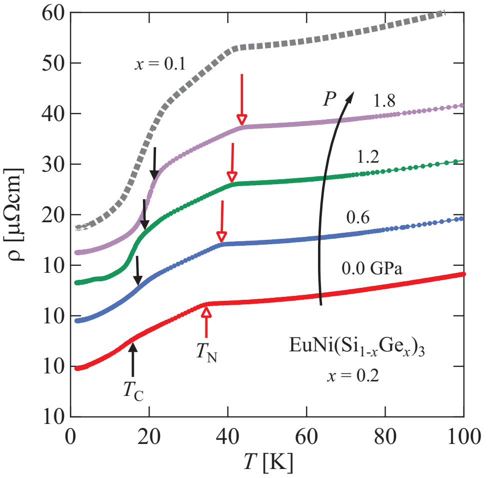

Figure 1: Temperature dependence of the electrical resistivity ρ of EuNi(Si$_{0.8}$Ge$_{0.2}$)$_3$ under pressures up to 1.8 GPa at temperatures from 2 to 100 K. The dotted line indicates $\rho(T)$ of EuNi(Si$_{0.9}$Ge$_{0.1}$)$_3$ at ambient pressure. The data are shifted up for eyes.

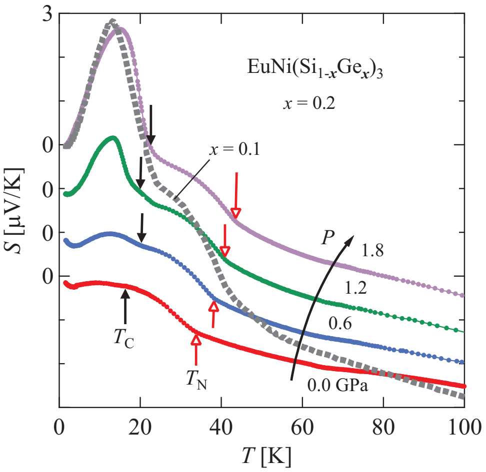

Figure 2: Temperature dependence of the thermopower S of EuNi(Si$_{0.8}$Ge$_{0.2}$)$_3$ under pressures up to 1.8 GPa at temperatures from 2 to 100 K. The dotted line indicates $S(T)$ of of EuNi(Si$_{0.9}$Ge$_{0.1}$)$_3$ at ambient pressure. The data are shifted up for eyes.

measurements, the applied pressure was estimated from the load on piston of the pressure cell at room temperature.

3 Results and Discussion

Figure 1 shows the temperature dependence of the electrical resistivity ρ of EuNi(Si$_{0.8}$Ge$_{0.2}$)$_3$ under pressures up to P = 1.8 GPa at the temperature region from 2 to 100 K. As shown in Fig. 1, ρ increases with increasing temperature, showing anomalies in the form of kink at the magnetic transition temperatures of $T_C \approx 16$ K and $T_N \approx 34$ K, and shows a linear increase with further increasing temperature. Both T_C and T_N, pointed by the solid and open arrows, respectively, in Fig. 1, increase with increasing pressure. As can be seen in Fig. 1, the temperature variation of ρ of EuNi(Si$_{0.8}$Ge$_{0.2}$)$_3$ at P = 1.8 GPa is very similar to that of EuNi(Si$_{0.9}$Ge$_{0.1}$)$_3$ at ambient pressure, which is indicated by the dotted line. This result reveals that the pressure effect on ρ is opposite to that of the substitution of Si by Ge in EuNi(Si$_{1-x}$Ge$_x$)$_3$ system.

Figure 2 depicts temperature dependence of the thermopower S of EuNi(Si$_{0.8}$Ge$_{0.2}$)$_3$ under selected pressures up to 1.8 GPa. At ambient pressure, S decreases with increasing temperature, taking a minimum at $T \approx 3.5$ K and a maximum at $T \approx 10$ K, and shows shoulder-like behavior at $T_C \approx 16$ K and an additional anomaly in the form of kink at $T_N \approx 34$ K. S decreases monotonically with further increasing temperature. At the pressure of $P \approx 1.0$ GPa, a maximum value of S at low temperature region changes its sign from negative to positive. Finally, S at P = 1.8 GPa also shows almost the same temperature variation as that of EuNi(Si$_{0.9}$Ge$_{0.1}$)$_3$ at ambient pressure, indicated by the dotted line in Fig. 2. In the low-temperature limit, the

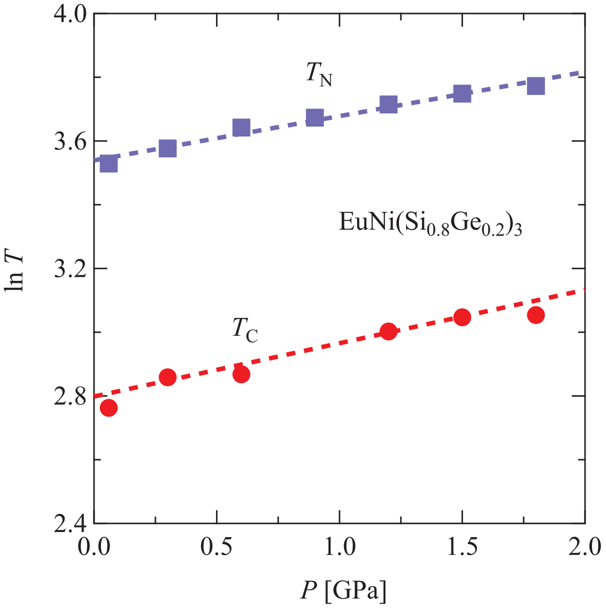

Figure 3: Pressure dependences of the magnetic transition temperatures of T_N and T_C of EuNi($Si_{0.8}Ge_{0.2}$)$_3$ in the form of $\ln T_m$ vs. P. The dashed lines are the results of the line fittings to the experimental data.

thermopower S for metallic conductor is expressed by the Mott's formula:

$$S(T) = -\frac{\pi^2 k_B^2}{3|e|} T \left(\frac{1}{\sigma} \frac{\partial \sigma}{\partial \varepsilon} \right)_{\varepsilon=\varepsilon_F},$$

where e, k_B and σ are the electronic charge, the Boltzmann constant and the spectral electrical conductivity, respectively [10, 11, 12]. The spectral conductivity σ is connected with the electronic density of states (DOS) in the vicinity of the Fermi level [13]. Thus, the low temperature behaviors of ρ and S, mentioned above, indicate the resemblance between the feature of DOS around the Fermi level in EuNi($Si_{0.8}Ge_{0.2}$)$_3$ at $P = 1.8$ GPa and that in EuNi($Si_{0.9}Ge_{0.1}$)$_3$ at ambient pressure.

Figure 3 shows the pressure dependences of the magnetic transition temperatures of T_N and T_C, obtained from $\rho(T)$ and $S(T)$ curves of EuNi($Si_{0.8}Ge_{0.2}$)$_3$, in the form of $\ln T_N$ ($\ln T_C$) vs. P. As shown in Fig 3, both T_N and T_C increase linearly with increasing pressure at the rate of $d \ln T_N/dP \approx 0.14$ GPa^{-1} and $d \ln T_C/dP \approx 0.2$ GPa^{-1}, respectively, which are almost the same values as those of EuNiSi$_3$, reported previously in Ref. [5]. We reported that the magnetic transition temperatures of T_N and T_C in EuNi($Si_{1-x}Ge_x$)$_3$ system depend strongly on the change of the atomic volume V induced by the atomic substitution of Si by Ge [7]. Correspondingly, we assume that the pressure dependences of T_N and T_C of EuNi($Si_{0.8}Ge_{0.2}$)$_3$ can be expressed by using the following Grüneisen parameters Ω_{T_N} and Ω_{T_C}, respectively,

$$\Omega_{T_N} = -\frac{d \ln T_N}{d \ln V} = \frac{1}{\kappa} \frac{d \ln T_N}{dP}, \quad (1)$$

$$\Omega_{T_C} = -\frac{d \ln T_C}{d \ln V} = \frac{1}{\kappa} \frac{d \ln T_C}{dP}. \quad (2)$$

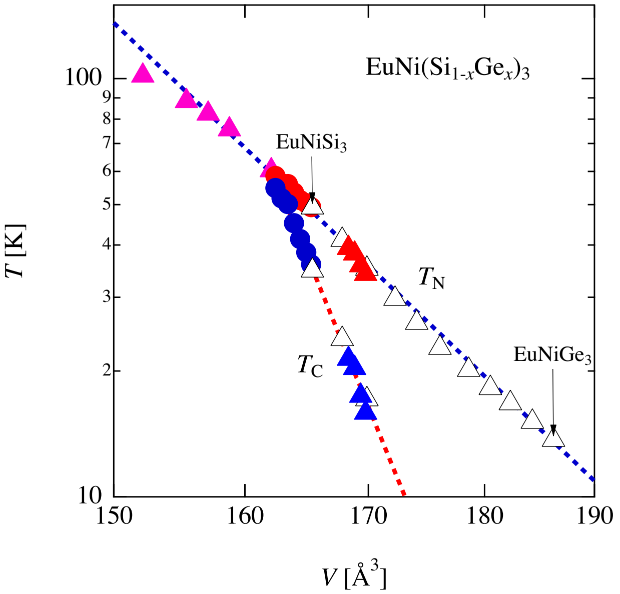

Figure 4: Atomic volume V dependences of the magnetic transition temperatures T_N and T_C of EuNi($Si_{1-x}Ge_x$)$_3$ compounds in double logarithmic scale. The pressure is transformed into the change of the atomic volume according to Eqs. (1) and (2).

Here, $\kappa = -\mathrm{d}\ln V/\mathrm{d}P$ is the compressibility of EuNi($Si_{0.8}Ge_{0.2}$)$_3$. The Grüneisen parameters Ω_{T_N} and Ω_{T_C} can be obtained from the results of the Ge composition x dependences of T_N, T_C, and V (the lattice parameters) [7]. Then we can determined the value of the compressibility κ, which is assumed as a constant for whole range of x in EuNi($Si_{1-x}Ge_x$)$_3$. The reasonable value of the compressibility for EuNi($Si_{1-x}Ge_x$)$_3$ system, $\kappa \approx 1.1 \times 10^{-2}$ GPa^{-1}, was obtained by using the values of $\mathrm{d}\ln T_N/\mathrm{d}P$ and $\mathrm{d}\ln T_C/\mathrm{d}P$, obtained from the line fittings to the plots of $\ln T_N$ and $\ln T_C$ vs. P, shown in Fig. 3. This value is consistent with that of $\kappa \approx 1.4 \times 10^{-2}$ GPa^{-1} for EuPtP [14] and of $\kappa \approx 1.0 \times 10^{-2}$ GPa^{-1} for RCo_2 (R: rare earths) system [15], for example.

The plots of T_N and T_C against the atomic volume V in double logarithmic scale are shown in Fig. 4. The results of the pressure measurements for the compounds with $x = 0$ and 0.2 are also indicated by solid symbols, where the pressure P is transformed into the change of the atomic volume according to Eqs. (1) and (2). The plots of T_N and T_C vs. V in double logarithmic scale lie on the individual dashed straight line, as shown in Fig. 4, revealing the validity of Eqs. (1) and (2). It is found that the effect of the increase of Si concentration on T_N and T_C is the same as that of the application of high pressure, resulting increase of T_N and T_C. These results indicate that the change of the atomic volume due to the atomic replacement or the applying pressure is responsible for the changes of the magnetic transition temperatures T_N and T_C. From the plots of T_N and T_C against V in Fig. 4, it is reasonable to consider that T_C and T_N merge together at $V_c \approx 162$ Å^3, and only the antiferromangetic phase transition, instead of the ferromagnetic one [6], was observed in the region below V_c. Further study is necessary to clarify the magnetic state of $EuNiSi_3$ under high pressure.

In summary, we have measured the electrical resistivity and thermopower of EuNi($Si_{0.8}Ge_{0.2}$)$_3$, which is a compound near to the phase boundary between the ferromagnetic and antiferromagnetic in the phase diagram for EuNi($Si_{1-x}Ge_x$)$_3$ system, under pressures up to 1.8 GPa at temperatures from 2 to 300 K. The magnetic transition temperatures T_N and T_C of EuNi($Si_{0.8}Ge_{0.2}$)$_3$ increase with increasing pressure. The pressure dependences of T_N and T_C are expressed by the Grüneisen parameters, which means that the changes of T_N and T_C of EuNi($Si_{1-x}Ge_x$)$_3$ system are strongly connected with the change of the atomic volume induced by the applying pressure or the atomic substitution. We obtained the reasonable value of the compressibility, $\kappa = 1.1 \times 10^{-2}$ GPa^{-1}, for EuNi($Si_{1-x}Ge_x$)$_3$ system by using the Grüneisen parameters for T_N and T_C.

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