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Observation of Hybridization Gap in Heavy Fermion System $EuNi_2(P_{1-x}Ge_x)_2$ via Point-Contact Spectroscopy

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We performed a point-contact spectroscopy (PCS) investigation in $EuNi_2(P_{0.8}Ge_{0.2})_2$ to examine the variation of an indirect hybridization gap by Ge substitution for P in $EuNi_2P_2$. The PCS spectrum exhibits an asymmetric double peak structure near the zero bias at T = 6 K. When the temperature is increased, the double peak structure shifts to low energy side. The temperature dependence of the PCS spectra can be reproduced by the theoretical model, indicating that the double peak structure originates from the indirect hybridization gap formed in the electronic density of states. Moreover, the indirect hybridization gap in $EuNi_2(P_{0.8}Ge_{0.2})_2$ is smaller than that in $EuNi_2P_2$. The results demonstrate the emergence of the indirect hybridization gap in $EuNi_2(P_{0.8}Ge_{0.2})_2$ and the suppression of the gap separation by Ge substitution

KEYWORDS: Heavy Fermion, *c-f* hybridization, Eu-compound, Point-contact spectroscopy

1. Introduction

Rare earth compounds have attracted considerable interest from the condensed matter community because they exhibit fascinating phenomena, such as Kondo effect, heavy fermion (HF) behavior, valence fluctuation, unconventional superconductivity, and non-Fermi liquid behavior [1, 2]. The hybridization between conduction and *f* electrons (*c-f* hybridization) gives rise to the delocalization of *f* electrons, which plays a key role in understanding the above phenomena. Theoretical studies have shown that the electronic density of states (DOS) near the Fermi energy in HF systems changes significantly as HF coherence evolves owing to the *c-f* hybridization. As the temperature decreases, a sharp peak arising from the Kondo resonance of the localized *f* moments screened by the conduction electrons splits into two peaks due to the development of the indirect hybridization gap in the DOS [3, 4], where the indirect gap is much smaller than the direct gap. Scanning tunneling spectroscopy (STS) and point-contact spectroscopy (PCS) through differential conductance measurements, which have been utilized to investigate the DOS in HF systems, confirm the evolution of the DOS predicted by a theoretical study [5-9].

We focus on the Eu based system $EuNi_2(P_{1-x}Ge_x)_2$ to examine the variation of an

indirect hybridization gap by changing the ground state properties. In the case of $x = 0$, it is revealed that $EuNi_2P_2$ exhibits an intermediate valence state at low temperatures, which comes from a strong *c-f* hybridization. In addition, the electronic specific heat coefficient of $EuNi_2P_2$ is ~ 100 mJ/(K^2mol) [10], indicating the formation of HF state at low temperatures. Meanwhile, $EuNi_2Ge_2$ shows antiferromagnetic order at $T_N \approx 30$ K with a stable divalent Eu state, meaning a weak *c-f* hybridization [11]. These features suggest that the Ge substitution for P in $EuNi_2P_2$ would lead to a reduction of the *c-f* hybridization. Recently, Paramanik *et al*., succeeded in the growth of $EuNi_2(P_{1-x}Ge_x)_2$ single crystals, and revealed that the increase of the Ge concentration gradually changes the ground state from paramagnetic HF state to antiferromagnetic ordered state [12]. However, the detailed variations of the electronic DOS with increasing the Ge concentration are not yet clarified.

In this study, we utilize the PCS technique to explore the DOS near the Fermi energy in 4*f*-electron compounds through the differential conductance measurements [13]. Actually, based on the PCS investigation, we observed the asymmetric double peak structure originating from the indirect hybridization gap in $EuNi_2P_2$ [9]. Furthermore, the decrease of the indirect hybridization gap with increasing temperature was observed clearly. These results strongly suggest that the PCS technique can capture the variation of the indirect hybridization gap due to the Ge substitution effect in $EuNi_2(P_{1-x}Ge_x)_2$.

Here, we report the PCS investigation on $EuNi_2(P_{0.8}Ge_{0.2})_2$. The PCS spectrum shows an asymmetric double peak structure at $T = 6$ K, which shifts to low bias side with increasing temperature. These spectra can be reproduced by the theoretical model on the electron tunneling from a probe tip to a HF system, meaning that double peak structure comes from the indirect hybridization gap in $EuNi_2(P_{0.8}Ge_{0.2})_2$. Moreover, the indirect hybridization gap in $EuNi_2(P_{0.8}Ge_{0.2})_2$ is smaller than that in $EuNi_2P_2$, indicating the suppression of the gap separation and the decrease of the Kondo temperature by the Ge substitution.

2. Experimental detail

A single crystal sample of $EuNi_2(P_{0.8}Ge_{0.2})_2$ is grown by Sn-flux method, as detailed in Ref. 12. The photograph of the synthesized sample is shown in the inset of Fig. 1. Powder X-ray diffraction reveals that the sample crystallizes in the $ThCr_2Si_2$-type structure. To confirm the concentration of Ge *x* in the sample, we conducted energy dispersive X-ray (EDX) examinations and the *x* is estimated to be ~0.23. Moreover, from the electrical resistivity measurements, we quantified the residual resistivity at $T = 1.7$ K to be 74 μΩcm, and accordingly the residual resistivity ratio (300 K/1.7 K) to be 2.9, which is consistent with the previously reported value [12]. The magnetic property on $EuNi_2(P_{0.8}Ge_{0.2})_2$ was measured by a SQUID magnetometer (MPMS, Quantum Design). Figure 1 shows the temperature dependence of the magnetic susceptibility in $EuNi_2(P_{0.8}Ge_{0.2})_2$, where the external magnetic field $B_{ext} = 1$ T is applied parallel to the (001) sample plane. In the high temperature region from 300 K to 150K, the magnetic susceptibility follows the Curie-Weiss law. Meanwhile, as the temperature decreases below 150 K, the magnetic susceptibility deviates downward from the Curie-Weiss law, and then shows the hump structure at $T \sim 35$ K. The temperature dependence of the magnetic susceptibility in $EuNi_2(P_{0.8}Ge_{0.2})_2$ resembles that in $EuNi_2P_2$, while the hump structure in $EuNi_2P_2$ is observed at $T \sim 40$ K. Namely, the hump structure shifts to low

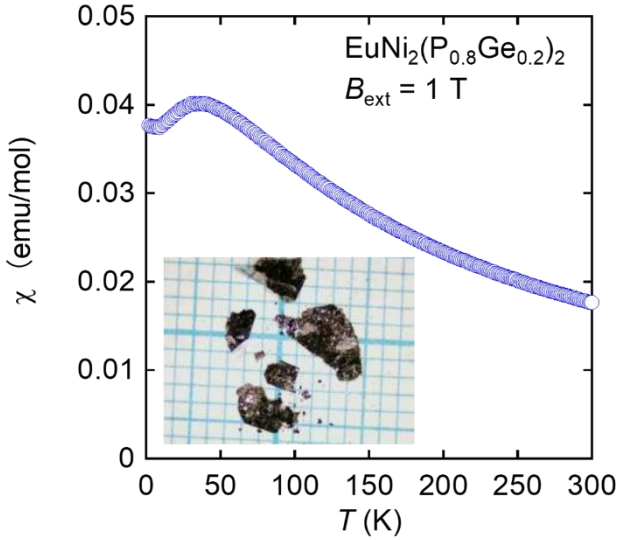

Fig. 1 The temperature dependence of the magnetic susceptibility in $EuNi_2(P_{0.8}Ge_{0.2})_2$. The external magnetic field B_{ext} = 1 T is applied parallel to the (001) sample plane. Inset shows the photograph of $EuNi_2(P_{0.8}Ge_{0.2})_2$ crystals grown by the Sn-flux method.

temperature by the Ge substitution, implying the suppression of the Kondo temperature.

PCS measurements were performed by utilizing a homemade PCS apparatus mounted in a low temperature cryostat. The PCS apparatus is composed of two types of the piezo devices: an attocube piezo-based positioner (ANPz51 attocube systems AG) and a stacked-type piezo-device, as detailed in [14]. These devices are installed for the precise control on the diameter of point contact formed between a probe tip and a sample from the atomic size to dozens of nanometers. Furthermore, utilizing the stacked-type piezo device controlled with a feedback loop enables to maintain a constant contact size during the temperature variation for the measurement. The Pt wire with a diameter of 0.2 mm is used for a probe tip. The differential conductance dI/dV spectra were measured using a lock-in technique with a modulation frequency of 2 kHz and a modulation voltage of ~ 0.5 mV.

3. Results and discussion

Figure 2(a) shows the dI/dV spectrum of $EuNi_2(P_{0.8}Ge_{0.2})_2$/Pt interface at T = 6.0 K. The asymmetric double peak is clearly observed at around ± 10 mV. The R_c represents the contact resistance, where the R_c is measured at V = 35 mV. Firstly, we discuss the heating effect near the point contact by applying the bias voltage. The PCS data possess a spectroscopic information only in the measurements carried out for the ballistic or diffusive regime. In other words, the PCS spectra reflects the electronic density of state only in the case of $d \leq l$, where d and l are a point contact diameter and an electron mean free path, respectively. In the thermal regime ($d >> l$), the conduction electrons accelerated by applying the bias voltage lose their energy due to the inelastic scattering, yielding an increase of the temperature near the point contact. According to the previous study [15], in the thermal regime, the voltage dependence of the differential resistance, i.e., dV/dI vs V, should be similar in shape to the temperature dependence of the electrical resistivity $\rho(T)$. Figure 2(b) shows the differential resistance recorded in the same

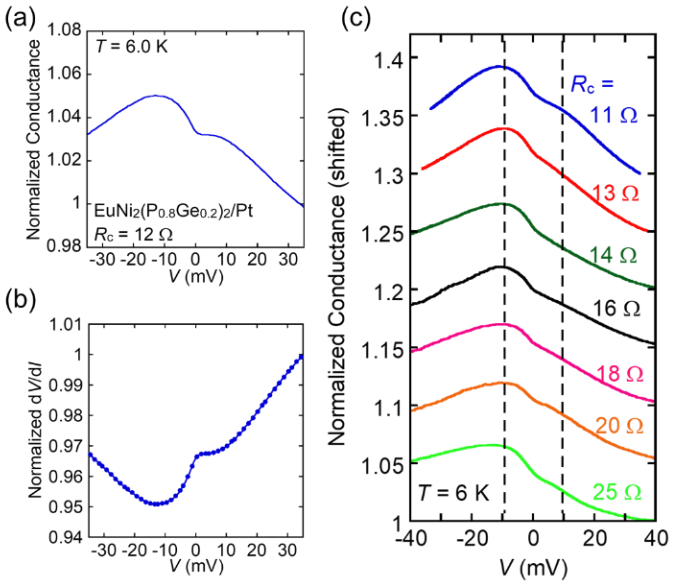

Fig. 2 (a) Differential conductance (dI/dV) spectrum of $EuNi_2(P_{0.8}Ge_{0.2})_2$/Pt interface at T = 6.0 K. (b) Differential resistance (dV/dI), which in recorded in the same measurement in (a). (c) Contact resistance dependence of the differential conductance of $EuNi_2(P_{0.8}Ge_{0.2})_2$/ Pt interface. The contact resistance is measured at V = 35 mV. The broken lines denote the peak position of the spectra, suggesting the peak position is largely unaffected by the contact resistance.

measurement in Fig. 2(a). The differential resistance represents a dip structure at around ± 10 mV. Meanwhile, the electrical resistivity of $EuNi_2(P_{1-x}Ge_x)_2$ decreases monotonically when the temperature is decreased from 100 K [12]. Hence, the asymmetric double peak structure in the PCS spectra cannot be attributed to the heating effect by applying the bias voltage.

The contact size dependence of the PCS spectra at $EuNi_2(P_{0.8}Ge_{0.2})_2$/Pt interface is shown in Fig. 2(c), where the increase of R_c corresponds to the decrease in the diameter of the point contact. The position of the asymmetric double peak structure is independent of the contact size. According to the previous study [16], the double peak structure arising from the elastic and/or inelastic scattering between conduction electron and structural disorder formed near the point contact shifts to high (or low) bias side when the contact size is varied. These results demonstrate that asymmetric double peak structure observed in the PCS spectra of $EuNi_2(P_{0.8}Ge_{0.2})_2$ is related to the electronic DOS not to the extrinsic origin such as structural disorder.

To reveal the origin of the asymmetric double peak structure, the temperature dependence of the PCS spectra at $EuNi_2(P_{0.8}Ge_{0.2})_2$/Pt interface is measured as shown in Fig. 3(a). As the temperature increases, the peak position shifts to low bias side, and then the double peak structure becomes unclear above ~ 30 K. The specific heat measurements of $EuNi_2(P_{1-x}Ge_x)_2$ revealed that the electronic specific heat coefficient is enhanced gradually with increasing the Ge concentration from x = 0 to x = 0.3 [12], indicating that the HF state is kept in the $EuNi_2(P_{0.8}Ge_{0.2})_2$ at low temperatures. Therefore, it is reasonable to fit the spectra by the theoretical model proposed by Maltseva *et al.*, (MDC model), which reproduces the tunneling spectra obtained between a probe tip and a Kondo lattice. In the electron tunneling process into Kondo lattice, there

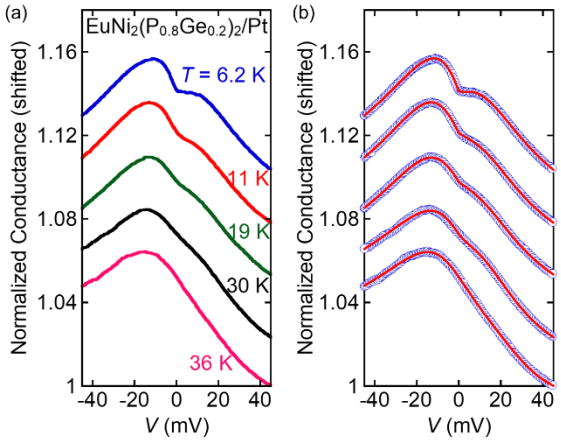

Figure 3 (a) Temperature dependence of the differential conductance (dI/dV) spectrum at $EuNi_2(P_{0.8}Ge_{0.2})_2$/Pt interface. (b) The fitting using MDC model for the spectra as shown in (a).

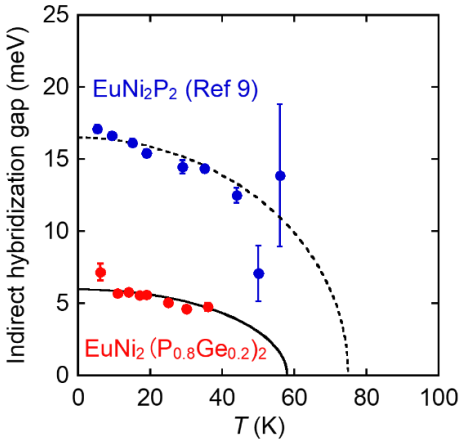

Figure 4 Temperature dependence of the indirect hybridization gap evaluated from the MDC model. The blue and red circles depict the date for $EuNi_2P_2$ [9] and $EuNi_2(P_{0.8}Ge_{0.2})_2$, respectively. The dashed and solid lines are fitting using eq. (1)

are two tunneling paths: tunneling into a localized state (a rare earth ion) and tunneling into a conduction band. Hence, an interference between the two tunneling paths occurs, resulting in the appearance of an asymmetric structure in the spectra. Moreover, when the coherence between the localized states develops, an asymmetric double peak structure emerges in a tunneling spectrum due to formation of an indirect hybridization gap near the Fermi level in the electronic DOS. The fitting using MDC model is depicted in Fig. 3 (b). The spectra can be reproduced by the MDC model, indicating that the asymmetric double peak structure originates from the indirect hybridization gap formed in the DOS. The value of the indirect hybridization gap evaluated from the fitting is shown in Fig. 4. The decrease of the indirect hybridization gap with increasing temperature is clearly visible. We fit the temperature dependence of the gap $\Delta_{hyb}(T)$ by the following equation

$$\Delta_{hyb} = \Delta_0 \sqrt{1 - \left(\frac{T}{T_0}\right)^2} \quad (1),$$

where the Δ_0 and T_0 are the indirect hybridization gap at T = 0 K and disappearance temperature of the indirect hybridization gap, respectively. As illustrated by a solid line in Fig. 4, the eq. (1) well reproduces the results, where 6 meV and 58 K are used as Δ_0 and T_0, respectively.

To clarify the Ge substitution effect on the indirect hybridization gap, we compare the PCS spectra of $EuNi_2(P_{0.8}Ge_{0.2})_2$ and these of $EuNi_2P_2$. As mentioned in the introduction, we carried out the PCS investigation on $EuNi_2P_2$, and observed the asymmetric double peak structure in the PCS spectra, which can be reproduced by MDC model [9]. By the fitting using eq. (1) for the temperature dependence of the indirect hybridization gap in $EuNi_2P_2$, Δ_0 and T_0 were estimated to be 16 meV and 73K, respectively, as shown as a dashed line in Fig. 4. In addition, we found that T_0 corresponds to the Kondo temperature of $EuNi_2P_2$ estimated by specific heat and thermal

expansion measurements [10]. From the results, we conclude that the Ge substitution leads to the suppression of the gap separation and the decrease of the Kondo temperature.

As described above, the PCS spectra in $EuNi_2(P_{0.8}Ge_{0.2})_2$ can be interpreted by the MDC model, indicating that the HF state in $EuNi_2(P_{0.8}Ge_{0.2})_2$ is developed due to evolution of the indirect hybridization gap. Moreover, our PCS results imply the approach to a quantum critical point (QCP) by increasing the Ge concentration. Further PCS investigations in high Ge concentration samples are indispensable for understanding the evolution of hybridization gap in the vicinity of a QCP.

4. Conclusion

We carried out the PCS measurements on $EuNi_2(P_{0.8}Ge_{0.2})_2$. The PCS spectra show an asymmetric double peak structure at T = 6 K, which shifts to low bias side with increasing temperature. These spectra can be interpreted by the theoretical model on the electron tunneling from a probe tip to a HF system, indicating that the indirect hybridization gap formed in $EuNi_2(P_{0.8}Ge_{0.2})_2$ is responsible for the double peak structure. Moreover, from the comparison of the PCS results between $EuNi_2P_2$ and $EuNi_2(P_{0.8}Ge_{0.2})_2$, we found the suppression of the gap separation and the decrease of the Kondo temperature by the Ge substitution.

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