Fermi Surface Properties of Eu-Divalent and Eu-Trivalent Electronic States with the AuCu₃-type Cubic Structure

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Abstract. The electronic states in EuBi₃ and EuPd₃ are known to be Eu-divalent and Eu-trivalent, respectively, from the previous studies using polycrystal samples. In the present study, we succeeded in growing high-quality single crystals, and carried out the de Haas-van Alphen (dHvA) measurements and energy band calculations to clarify the Fermi surface properties.

1. Introduction

The large lattice parameter of the Eu compound, compared with those of the corresponding other rare-earth compounds with the trivalent electronic state, is a good indication of the divalence of Eu. Namely, most of Eu compounds are in the divalent electronic state and order magnetically, similar to the corresponding Gd compound, revealing that the Eu-divalent (Eu²⁺) electronic state is stable compared with the Eu-trivalent (Eu³⁺) electronic state. We have recently clarified the Eu-divalent electronic states by measuring the magnetic susceptibility, magnetization, specific heat, and de Haas-van Alphen (dHvA) effect using high-quality single-crystal samples of EuGa₄ [1], EuBi₃ [2], and EuCd₁₁ [3].

On the other hand, there are a few Eu-trivalent compounds at ambient pressure. Among them, EuPd₃ is well known to be a Eu-trivalent compound. In fact, a single Mössbauer line was observed with a temperature-independent isomer shift (IS) of 4.5 ± 0.1 mm/s [4]. We have also clarified the Fermi surface properties of EuPd₃ by the dHvA experiments and energy band calculations [5].

Here we report in the present paper how largely the electronic properties are different between the Eu-divalent compound, EuBi₃ and a Eu-trivalent compound, EuPd₃ with the AuCu₃-type cubic structure.
2. Experimental

Single crystals of EuBi$_3$ were grown in a growing process of EuNi$_2$Ge$_2$ by the Bi-flux method [2], with a typical single size of (1-2) $\times$ (1-2) $\times$ (1-2) mm$^3$. Single crystals of EuPd$_3$ were, however, not grown by the flux method such as Pb, and then the Bridgeman technique was applied using the Mo crucible, which was heated up to 1450 °C and then slowly cooled to room temperature, taking 8 days [5]. The direction of the sample was determined by the X-ray Laue method.

The dHvA measurement was carried out by the standard field modulation method with a modulation frequency of 75 Hz and a modulation field of 90 Oe in strong magnetic fields up to 150 kOe.

3. Experimental results

Figure 1 shows the temperature dependence of the electrical resistivity in EuBi$_3$ and EuPd$_3$. The resistivity approximately decreases linearly with decreasing temperature, but orders antiferromagnetically below $T_N = 7.4$ K in EuBi$_3$, as shown in inset of Fig. 1. On the other hand, the resistivity is almost constant below 15 K in EuPd$_3$, indicating no magnetic ordering.

A striking difference between EuBi$_3$ and EuPd$_3$ is reflected in magnetization. A low-temperature magnetization in EuBi$_3$ increases linearly with increasing a magnetic field, indicating a simple canting process of magnetization, and reaches a full magnetic moment of 7 $\mu_B$ ($4f^7$: $S = 7/2$, $L = 0$ and $J = 7/2$), as shown in inset of Fig. 2. Figure 2 shows a relation of $H_c$ vs $T_N - \theta_p$ in some Eu compounds including EuBi$_3$. A solid line corresponds to $H_c = (k_B/3\mu_B)/(T_N - \theta_p)$, where $H_c$ is a critical field reaching 7 $\mu_B$/Eu, $T_N$ is the Néel temperature, and $\theta_p$ is the paramagnetic Curie temperature. In the case of EuPd$_3$, the magnetization is small because of the trivalent electronic state ($4f^6$: $S = L = 3$ and $J = 0$), but can be not neglected because of the contribution of a Van - Vleck susceptibility based on the $J$-multiplets, $7F$ with $J = 0$ to 6 [6].

We clarified the Fermi surface properties by the dHvA experiments and energy band calculations for EuBi$_3$ and EuPd$_3$. Figure 3 shows the angular dependences of the dHvA frequencies in EuBi$_3$, the corresponding theoretical ones in SrBi$_3$, and theoretical Fermi surfaces of SrBi$_3$. Here, the dHvA frequency $F = (ehS_F/2\pi\epsilon)$ is proportional to the maximum or minimum cross-sectional area of the Fermi surface $S_F$, which is shown as a unit of magnetic
Figure 2. Relation between the critical field $H_c$ and $T_N - \theta_p$.

Figure 3. Angular dependences of (a) the dHvA frequencies in EuBi$_3$ and (b) the theoretical ones in SrBi$_3$, together with (c) the theoretical Fermi surfaces, cited from ref. [2].
field $H$. Several dHvA branches named $\alpha$, $\beta$, $\gamma$, $\delta_i$, and $\varepsilon_i$ ($i=1\text{-}3$) are observed. All the branches are closed. If we assume three branches named $\alpha$, $\beta$, and $\gamma$ to be spherical, the volume of the Fermi surface is $0.28 \, V_B$ for branch $\alpha$, $0.14 \, V_B$ for branch $\beta$, and $0.12 \, V_B$ for branch $\gamma$, being $0.54 \, V_B$ in total, where $V_B$ is the volume of the Brillouin zone. These Fermi surfaces are bands 8 and 9-hole Fermi surfaces shown in Fig. 3(c). The dHvA branches $\delta_i$ and $\varepsilon_i$ ($i=1\text{-}3$) with small dHvA frequencies are due to small band 10-electron Fermi surfaces. The cyclotron effective masses are small, being in the range from 0.54 to $1.8 \, m_0$ ($m_0$: rest mass of an electron). The dHvA branches in EuBi$_3$ are thus well explained by the energy band calculation based on the local density approximation (LDA) for a non-$4f$ reference compound SrBi$_3$.

Next we show in Figs. 4(a) and 4(b) the dHvA oscillations in EuPd$_3$ for $H \parallel \langle 110 \rangle$, and the corresponding fast Fourier transformation (FFT) spectrum, respectively. Two dHvA branches named $\delta$ and $\zeta$ are observed. We rotated the sample against the magnetic field and obtained the angular dependences of the dHvA frequencies, as shown in Fig. 5(a). Detected dHvA branches named $\alpha$, $\beta$, $\gamma$, $\delta$, $\varepsilon$, and $\zeta$ are well explained in the LDA + $Ud$- scheme for EuPd$_3$, as shown in Figs. 5(b) and 5(c). Here, the $4f$ orbitals are treated to be widely separated from the Fermi energy by introducing the screened Coulomb parameter $U = 0.4$ Ry. Furthermore, the Pd-$4d$ electrons are slightly shifted down by 0.03 Ry so as to eliminate the flat bands based on the Pd-$4d$ electrons. The experimental results in Fig. 5(a) are in good agreement with the theoretical ones in Fig. 5(b). The cyclotron masses are in the range from 0.3 to $1.0 \, m_0$.

4. Concluding remark

We presented mainly the Fermi surfaces in a Eu-divalent compound, EuBi$_3$ and a Eu-trivalent compound, EuPd$_3$, emphasizing that the dHvA branches in EuBi$_3$ are well explained by the results of energy band calculations (LDA) for a non-$4f$ reference compound SrBi$_3$, and these in

![Figure 4](image-url)

**Figure 4.** (a) Typical dHvA oscillations and (b) the corresponding FFT spectrum for $H \parallel \langle 110 \rangle$ in EuPd$_3$.  

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Figure 5. Angular dependences of (a) the dHvA frequencies in EuPd$_3$ and (b) the theoretical ones in EuPd$_3$ (LDA + $Ud^-$), together with (c) the theoretical Fermi surfaces, cited from ref. [5].

Figure 6. Relation between the Néel temperature $T_N$ and the lattice constant $a$ in EuX$_3$ (X: Bi, Pb, Sn, Pd).
EuPd$_3$ are also in excellent agreement with the results of energy band calculations based on the LDA + $U_d$ - scheme for EuPd$_3$.

Finally we remark the lattice parameters in EuBi$_3$ and EuPd$_3$ with the AuCu$_3$-type cubic structure. Figure 6 shows a relation between the Neel temperature and the lattice constant \(a\). Note that the right hand is short in scale, considering the well-known Doniach phase diagram. It is noticed that the lattice constant of EuPd$_3$ is extremely short, compared with these in the other Eu-divalent compounds, EuBi$_3$, EuPb$_3$, and EuSn$_3$ with the AuCu$_3$-type cubic structure. A smooth connection is not realized between EuSn$_3$ and EuPd$_3$, most likely revealing a valence transition with the first order.

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