Mass Enhancement of Nearly Trivalent Compound EuCo$_2$Si$_2$: Studied by the de Haas-van Alphen Experiments and Energy Band Calculations

Yoshichika Ônuki$^1$, Ai Nakamura$^2$, Dai Aoki$^{3,4}$, Mounir Boukahil$^4$, Yoshinori Haga$^5$, Tetsuya Takeuchi$^6$ Hisatomo Harima$^7$, Masato Hedo$^1$ and Takao Nakama$^1$

$^1$Faculty of Science, University of the Ryukyus, Nishihara, Okinawa 903-0213, Japan
$^2$Graduate School of Engineering and Science, University of the Ryukyus, Nishihara, Okinawa 903-0213, Japan
$^3$Institute for Materials Research, Tohoku University, Oarai, Ibaraki 311-1313, Japan
$^4$INAC/SPSMS, CEA-Grenoble, 17 rue des Martyrs 38054 Grenoble, France
$^5$Advanced Science Research Center, Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-1195, Japan
$^6$Low temperature Center, Osaka University, Toyonaka, Osaka 560-0043, Japan
$^7$Graduate School of Science, Kobe University, Kobe 657-8501, Japan

E-mail: onuki@phys.u-ryukyu.ac.jp

Abstract. We succeeded in growing single crystals of EuCo$_2$Si$_2$ by the Bridgman method, and carried out the de Haas-van Alphen (dHvA) experiments. EuCo$_2$Si$_2$ was previously studied from a viewpoint of the trivalent electronic state on the basis of the magnetic susceptibility and X-ray absorption experiments, whereas most of the other Eu compounds order magnetically, with the divalent electronic state. The detected dHvA branches in the present experiments are found to be explained by the results of the full potential linearized augmented plane wave energy band calculations on the basis of a local density approximation (LDA) for YCo$_2$Si$_2$ (LDA) and EuCo$_2$Si$_2$ (LDA + $U$), revealing the trivalent electronic state. The detected cyclotron effective masses are moderately large, ranging from 1.2 to 2.9 $m_0$.

1. Introduction

Large lattice parameters of the Eu compound, compared with those of the other rare earth compounds with the trivalent electronic state, are a good indication of the divalence of Eu. Most of the Eu intermetallic compounds are in the divalent electronic state, revealing that the Eu-divalent (Eu$^{2+}$) electronic state is stable compared with the Eu-trivalent (Eu$^{3+}$) state. An energy difference between the Eu$^{2+}$ and Eu$^{3+}$ states is, however, not so large [1]. Therefore, the valence transition occurs in some Eu compounds, namely from a divalent state of Eu$^{2+}$ ($4f^7$: $S = 7/2$, $L = 0$, and $J = 7/2$) at high temperatures to a nearly trivalent state ($4f^6$: $S = L = 3$ and $J = 0$) at low temperatures, as in EuPd$_2$Si$_2$ [2]. Here, $S$, $L$, and $J$ are spin, orbital, and total angular momentum, respectively. The valence transition is also accelerated by applying pressure, as in EuRh$_2$Si$_2$ [3].

We recently studied the Eu-divalent electronic states by measuring the de Haas-van Alphen (dHvA) effect using high-quality single crystal samples of EuGa$_4$ [4], EuBi$_3$ [5], and EuCd$_{11}$ [6].
These compounds order antiferromagnetically, as in Gd compounds. The Fermi surface properties in these compounds are found to be well explained by the results of energy band calculations for the corresponding non-4f divalent-Sr compounds.

On the other hand, the trivalent electronic states are not clarified yet in a viewpoint of the Fermi surface properties. There exist a few Eu-trivalent compounds at ambient pressure, such as EuPd$_3$ and EuCo$_2$Si$_2$. Very recently we clarified the Fermi surface properties of EuPd$_3$ [7]. The dHvA branches detected in the dHvA experiments are well explained by the results of the full potential linearized augmented plane wave (FLAPW) energy band calculations based on a local density of approximation (LDA) with additional treatments. Another compound of EuCo$_2$Si$_2$ with the ThCr$_2$Si$_2$-type tetragonal structure was also studied from a viewpoint of the trivalent electronic state, measuring the Van Vleck-type magnetic susceptibility based on the $J$-multiplets, $^7F_J$, electrical resistivity, specific heat and X-ray absorption [8].

In the present paper, we grew single crystals of EuCo$_2$Si$_2$ by the Bridgman technique, and carried out the dHvA experiments to clarify the Fermi surface properties. The dHvA data are compared with the results of energy band calculations.

2. Experimental

EuCo$_2$Si$_2$ single crystals were grown by the Bridgman technique. Starting materials of 3N-Eu, 4N-Co and 6N-Si with the constitution of Eu:Co:Si=1.1:2:2, were inserted in a Mo-crucible, which was sealed using a tetra-arc furnace. The Mo crucible was heated up to 1480 °C and then slowly cooled to room temperature. The direction of the sample was determined from the X-ray Laue method. We also determined at room temperature the lattice parameters and the site positions of atoms in EuCo$_2$Si$_2$ using a small single crystal, as summarized in Table 1. The measurements were performed on an imaging plate area detector with graphite monochromated Mo-K$_\alpha$ radiation.

As the single crystal sample of EuCo$_2$Si$_2$ is of a thin plate, the cantilever dHvA measurements were applied to EuCo$_2$Si$_2$, with a modulation frequency of 15.4 Hz, and modulation field of 100 Oe in magnetic fields up to 150 kOe, as shown in Fig. 1(a).

Table 1. Lattice parameters and the site positions of atoms at room temperature in EuCo$_2$Si$_2$.

|      | $a$  | $c$  |
|------|------|------|
|      | 3.91953(9) Å | 9.8327(2) Å |

|          | x    | y    | z    |
|----------|------|------|------|
| Eu       | 0    | 0    | 0    |
| Co       | 1/2  | 0    | 1/4  |
| Si       | 0    | 0    | 0.3716(3) |

3. Experimental results

We show in Fig. 1(b) the dHvA oscillations of EuCo$_2$Si$_2$ for the magnetic field tilted by 9° from [001] to [110] at 0.1 K. Four dHvA branches were observed, named $\alpha$, $\beta$, $\gamma$, and $\delta$ in the fast Fourier transformation (FFT) spectrum, as shown Fig. 1(c). The angular dependences of the dHvA frequencies are shown in Fig. 2(a). Here, the dHvA frequency $F (=chS_F/2\pi e)$ is proportional to the maximum or minimum cross-sectional area $S_F$, which is shown in unit of magnetic field $H$.

Figures 2(b), 2(c), and 2(d) show the theoretical angular dependences of the dHvA frequencies for YCo$_2$Si$_2$, EuCo$_2$Si$_2$ based on the standard LDA, and EuCo$_2$Si$_2$ based on LDA + $U$, respectively.
Figure 1. (a) Single-crystal sample on the cantilever dHvA apparatus, (b) typical dHvA oscillations, and (b) the corresponding FFT spectrum in EuCo$_2$Si$_2$.

respectively. Here, the lattice parameters and the site positions in Table 1 were adopted in these band calculations. Note that branch $\beta$ is not detected for $H \parallel [001]$. This is mainly due to the damping of the dHvA signal based on the curvature factor of branch $\beta$. The dHvA signal is also weaken for the symmetrical direction in the present cantilever dHvA measurement. The corresponding Fermi surfaces and densities of states are shown in Figs. 3 and 4, respectively.

When we compare the experimental result in Fig. 2(a) with the theoretical results in Fig. 2(b), 2(c), and 2(d), the EuCo$_2$Si$_2$ (LDA + $U$) model is well applicable to the experimental result, although branch $\beta$ is large in the dHvA frequency. Note that the EuCo$_2$Si$_2$ (LDA + $U$) model is very similar to the YCo$_2$Si$_2$ (LDA) model. On the other hand, the EuCo$_2$Si$_2$ (LDA) model is rather good as for branch $\beta$, although branch $\delta$ is large in the dHvA frequency. Important are the 4$f$ level in the band and the contribution of 4$f$ electrons to the density of states and Fermi surfaces. We will discuss the electronic specific heat coefficient $\gamma$.

It is stressed that in EuCo$_2$Si$_2$ (LDA), 4$f$ electrons are located just above and below the Fermi energy $E_F$ and contribute to the density of states, as shown in Fig. 4(b), indicating a large theoretical electronic specific heat coefficient $\gamma_b = 19.1$ mJ/(K$^2$.mol). Note that an experimental $\gamma$ value in EuCo$_2$Si$_2$ is 9.6 mJ/(K$^2$.mol) [8]. Here, introducing the screened Coulomb parameter $U$ is extremely effective for 4$f$-orbitals to achieve realistic band calculations. This was recently applied to EuPd$_3$ [7], as mentioned in Introduction. In the present case of EuCo$_2$Si$_2$ (LDA + $U$), as shown in Fig. 4(c), the corresponding 4$f$-orbitals are widely separated.
Figure 2. (a) Angular dependences of the dHvA frequencies in EuCo$_2$Si$_2$ and the theoretical ones in (b) YCo$_2$Si$_2$ (LDA), (c) EuCo$_2$Si$_2$ (LDA), and (d) EuCo$_2$Si$_2$ (LDA + U).
from the Fermi energy $E_F$ by introducing $U = 0.4$ Ry. The theoretical $\gamma_b$ for the LDA + $U$ treatment is 7.48 mJ/(K$^2$·mol), which is almost the same as $\gamma_b = 7.30$ mJ/(K$^2$·mol) in YCo$_2$Si$_2$ (LDA), shown in Fig. 4(a). Note that the experimental $\gamma$ value in YCo$_2$Si$_2$ is obtained to be 8.6±0.3 mJ/(K$^2$·mol), as shown in Fig. 5. Note that the 4$f$ level in EuCo$_2$Si$_2$ is located at 0.4 Ry, or 5.4 eV from the Fermi level, as shown in Fig. 4(c). This is reasonable in the trivalent electronic configuration, as in EuPd$_3$ [7]. Further note that $\gamma = 9.6$ mJ/(K$^2$·mol) in EuCo$_2$Si$_2$ is larger than $\gamma = 8.6±0.3$ mJ/(K$^2$·mol) in YCo$_2$Si$_2$, $\gamma_b = 7.30$ mJ/(K$^2$·mol) in YCo$_2$Si$_2$ (LDA), and $\gamma_b = 7.48$ mJ/(K$^2$·mol) in EuCo$_2$Si$_2$ (LDA + $U$). The present mass enhancement is not explained by the usual electron-phonon interaction, but is mainly due to the contribution of the 4$f$ electrons, via the hybridization between the 4$f$ electrons and the conduction electrons.

In the present case of EuCo$_2$Si$_2$, the results of band calculations for YCo$_2$Si$_2$ (LDA) and EuCo$_2$Si$_2$ (LDA + $U$) are approximately in agreement with the experimental results. The present dHvA branches are thus identified from the Fermi surfaces shown in Fig. 3(c), as follows:
1) Branch $\alpha$ is due to the band-28 hole Fermi surface.
2) Branch $\beta$ is due to an outer orbit of the band-27 hole Fermi surface.
3) Branch $\gamma$ is due to the band-29 electron Fermi surface.
4) Branch $\delta$ is due to an inner orbit of the band-27 hole Fermi surface.

**Figure 3.** Theoretical Fermi surfaces in (a) YCo$_2$Si$_2$ (LDA), (b) EuCo$_2$Si$_2$ (LDA), and (c) EuCo$_2$Si$_2$ (LDA + $U$).
Figure 4. Theoretical densities of states in (a) YCo$_2$Si$_2$ (LDA), (b) EuCo$_2$Si$_2$ (LDA), and (c) EuCo$_2$Si$_2$ (LDA + U).

Figure 5. $T^2$-dependence of the specific heat $C$ in the form of $C/T$ in YCo$_2$Si$_2$.

We also determined the cyclotron effective mass, ranging from 1.2 to 2.9 $m_0$ in EuCo$_2$Si$_2$. The cyclotron masses and band masses are shown in Fig. 2. These are moderately large, when compared with the cyclotron masses ranging from 0.3 to 1.0 $m_0$ in a typical Eu$^{3+}$-compound EuPd$_3$.

4. Concluding Remark

The Fermi surface properties in EuCo$_2$Si$_2$ are approximately explained by the present band calculations for YCo$_2$Si$_2$ (LDA) and EuCo$_2$Si$_2$ (LDA + U). The trivalent electronic states in Eu compounds are, however, different in compounds. We show in Fig. 6 the temperature dependences of electrical resistivities in EuPd$_3$, EuCo$_2$Si$_2$, EuIr$_2$Si$_2$, and EuNi$_2$P$_2$, where the $\gamma$ values are 3.6, 9.6, 40, and 93 mJ/(K$^2$·mol), respectively. In the case of EuPd$_3$, no mass
Figure 6. Temperature dependences of the electrical resistivities in (a) EuPd$_3$, (b) EuCo$_2$Si$_2$, (c) EuIr$_2$Si$_2$, and (d) EuNi$_2$P$_2$.

enhancement is observed. Very recently, we clarified that a large electronic specific heat coefficient $\gamma = 93$ mJ/(K$^2$·mol) in EuNi$_2$P$_2$ is based on the Kondo effect. The 4$f$ electrons contribute to the conduction electrons in EuNi$_2$P$_2$, together with in EuIr$_2$Si$_2$. There exists also a small contribution of 4$f$ electrons to the conduction electrons even in EuCo$_2$Si$_2$, as discussed in the former section. Note that the electrical resistivity in EuCo$_2$Si$_2$ was explained by the resistivity model based on the trivalent electronic state [8]. The dHvA experiments for EuNi$_2$P$_2$ and EuIr$_2$Si$_2$ are left to the future study.

Acknowledgments
This work was supported by Grants-in-Aid for Scientific Research on Challenging Exploratory Research (No. 25610097) and (C) (No. 25400342) from the Ministry of Education, Culture, Sports, Science and Technology, Japan and ERC starting grant(NewHeavyFermion).

References
[1] Gschneidner, Jr, A K 1969 J. Less Common Metals 17 1
[2] Sampathkumaran E V, Gupta C L, Vijayaraghavan R, Gopalakrishanon V K, Pillay G R and Devare G H 1981 J. Phys. C: Solid State Phys. 14 L237
[3] Mitsuda A, Hamano S, Araoka N, Yayama H and Wada H 2012 J. Phys. Soc. Jpn. 81 023709
[4] Nakamura A, Hiranaka Y, Hedo M, Nakama T, Miura Y, Tsutsumi H, Mori A, Ishida K, Mitamura K,
Hirose Y, Sugiyama K, Honda F, Settai R, Takeuchi T, Hagiwara M, Matsuda D T, Yamamoto E, Haga Y, Matsubayashi K, Uwatoko Y, Harima H and Onuki Y 2013 J. Phys. Soc. Jpn. 82 104703

[5] Nakamura A, Hiranaka Y, Hedo M, Nakama T, Tatetsu Y, Maehira T, Miura Y, Mori A, Tsutsumi H, Hirose Y, Mitamura K, Sugiyama K, Hagiwara M, Honda F, Takeuchi T, Haga Y, Matsubayashi K, Uwatoko Y and Onuki Y 2013 J. Phys. Soc. Jpn. 82 124708

[6] Nakamura A, Hiranaka Y, Uejo T, Takeuchi T, Honda F, Harima H, Matsubayashi K, Uwatoko Y, Hedo M, Nakama T and Onuki Y 2014 J. Phys. Soc. Jpn. 83 074714

[7] Nakamura A, Takeuchi T, Harima H, Hedo M, Nakama T and Onuki Y 2014 J. Phys. Soc. Jpn. 83 053708

[8] Seiro S, Kummer K, Vyalikh D, Caroca-Canales N and Geibel C 2013 Phys. Status Solidi B 250 621