Fermi Surface and Magnetic Properties in
Ferromagnet CoS$_2$ and Paramagnet CoSe$_2$ with the
Pyrite-type Cubic Structure

A Teruya$^1$, F Suzuki$^1$, D Aoki$^2$, F Honda$^2$, A Nakamura$^2$,
M Nakashima$^2$, Y Amako$^3$, H Harima$^4$, K Uchima$^5$, M Hedo$^6$,
T Nakama$^6$, and Y Onuki$^8$

$^1$Graduate School of Engineering and Science, University of the Ryukyus, Nishihara, Okinawa 903-0213, Japan
$^2$Institute for Materials Research, Tohoku University, Oarai, Ibaraki 311-1313, Japan
$^3$Faculty of Science, Shinshu University, Matsumoto, Nagano 390-8621, Japan
$^4$Graduate School of Science, Kobe University, Kobe 657-8501, Japan
$^5$General Education, Okinawa Christian Junior College, Nishihara, Okinawa 903-0207, Japan
$^6$Faculty of Science, University of the Ryukyus, Nishihara, Okinawa 903-0213, Japan
E-mail: uchima@ocjc.ac.jp

Abstract. We succeeded in growing high-quality single crystals of pyrite-type cubic compounds CoSe$_2$ and CoS$_2$ using a transport agent of CoBr$_2$ and measured the electrical resistivity, specific heat, magnetic susceptibility, magnetization, and the de Haas–van Alphen (dHvA) effect. We confirmed that CoSe$_2$ is an exchange-enhanced paramagnet revealing a broad maximum at around 50 K in the temperature dependence of the magnetic susceptibility. The electronic specific heat coefficient is moderately large, $\gamma = 18$ mJ/(K$^2$.mol). On the other hand, CoS$_2$ is a ferromagnet with a Curie temperature $T_C = 122$ K and an ordered moment $\mu_B = 0.93$ $\mu_B/Co$. The $\gamma$ value of 21 mJ/(K$^2$.mol) in CoS$_2$ is slightly larger than that of CoSe$_2$. A large ordered moment, together with a large $\gamma$ value, is a characteristic feature in CoS$_2$ because CoS$_2$ is a half-metallic spin state in the ferromagnetic state. Correspondingly, we detected a main dHvA branch with a cyclotron effective mass of 13$m_0$ in the dHvA experiments. The detected dHvA branches in CoS$_2$ and CoSe$_2$ are discussed on the basis of the results of energy band calculations, revealing a broken four-fold-symmetry in the angular dependence of the dHvA frequency.

1. Introduction

CoS$_2$ and CoSe$_2$ belong to the pyrite-type compounds, which were once studied extensively and are still interestingly studied from a viewpoint of a magnetic transition under pressure [1] and the application of spintronics [2]. CoS$_2$ is a ferromagnet with a Curie temperature $T_C = 124$ K. In CoS$_2$, the antibonding Co-$e_g$ band is occupied by one 3$d$ electron, revealing a quarter filling. An ordered moment of $\mu_s = 0.85$ $\mu_B/Co$ with an easy-axis along the [111] direction in CoS$_2$ is close to 1 $\mu_B/Co$ in a low-spin state of Co$^{2+}$ ($S = 1/2$ and $g = 2$). In fact, the magnetic susceptibility follows the Curie–Weiss law above 400 K, with an effective magnetic moment of $\mu_{eff} = 1.76$ $\mu_B/Co$, which corresponds to 1.73 $\mu_B$ of Co$^{2+}$ [3, 4]. The de Haas–van Alphen (dHvA) experiment was carried out, detecting the mainly five kinds of dHvA branches.
with the largest cyclotron mass of about $5m_0$ [5]. On the other hand, CoSe$_2$ is an exchange-enhanced paramagnet. The magnetic susceptibility follows the Curie–Weiss law above 300 K, with $\mu_{\text{eff}} = 1.72 \mu_B$/Co [3], which also corresponds to 1.73 $\mu_B$/Co of Co$^{2+}$. These characteristic features including the temperature-induced local moments at high temperatures and itinerant 3$d$-electrons at low temperatures are explained by the spin fluctuation theory [6].

In the present dHvA experiments, we detected a large cyclotron effective mass $m^*_c = 13m_0$ for a main Fermi surface of CoS$_2$. This is unexpectedly large because CoS$_2$ possesses a large ordered moment. The cyclotron mass of CoS$_2$ is compared with that of CoSe$_2$. The Fermi surfaces obtained from the angular dependences of dHvA frequencies in CoS$_2$ and CoSe$_2$ are also compared with the results of energy band calculations.

2. Experimental Procedure

Single crystals of CoS$_2$ were previously grown by the vapor transport method using the chlorine (Cl$_2$) gas [4, 5]. Recently, CoBr$_2$ was employed as a transport agent [7], revealing the residual resistivity $\rho_0 = 0.86 \mu \Omega \cdot \text{cm}$ and the residual resistivity ratio RRR[= $\rho_{RT}/\rho(5 \text{ K})]$ = 160. The CoS$_2$ powder was set in a hot zone at 700 °C and single crystals were grown in a cold zone at 640 °C. Following this method, we grew single crystals of CoS$_2$ with 3–4 mm on an edge. The best sample was obtained with $\rho_0 = 0.42 \mu \Omega \cdot \text{cm}$ and RRR = 410. Note that RRR was estimated to be 60 in the vapor transport method using Cl$_2$ in the previous report [4, 5]. Under the same experimental condition, we also grew single crystals of CoSe$_2$. As far as we know, the previous measurements of CoSe$_2$ were carried out using polycrystalline samples. The present results shown below were the first ones using single crystal samples. The direction of the sample was determined by the X-ray Laue method.

The electrical resistivity was measured by the conventional four-terminal DC method. The magnetic susceptibility and the magnetization were measured using a commercial superconducting quantum interference device (SQUID) magnetometer. The specific heat was measured by the quasi-adiabatic heat-pulse method. The dHvA experiment was carried out by the standard field-modulation method with a modulation frequency of 60 Hz and a modulation field of 80 Oe in strong magnetic fields up to 150 kOe.

3. Experimental Results

First, we confirmed the fundamental properties of a paramagnet CoSe$_2$ and a ferromagnet CoS$_2$ measuring the electrical resistivity, specific heat, magnetic susceptibility, and magnetization. Figure 1(a) shows the temperature dependence of the electrical resistivity for the current along the [100] direction. The resistivity in CoSe$_2$ decreases almost linearly with decreasing temperature. The $\rho_0$ and RRR are $\rho_0 = 2.1 \mu \Omega \cdot \text{cm}$ and RRR = 49, revealing a relatively good single crystal sample.

Next, we measured the specific heat $C$ below 15 K. Figure 1(b) shows the $T^2$-dependence of the specific heat in the form of $C/T$. The specific heat in CoSe$_2$ consists of the electronic specific heat $\gamma T$ and phonon contribution $C_{\text{ph}} = \beta T^3$ because the magnetic susceptibility becomes approximately constant below 15 K, shown below. The electronic specific heat coefficient $\gamma$ and the Debye temperature $\Theta_D$ are obtained as $\gamma = 18 \text{ mJ}/(\text{K}^2 \cdot \text{mol})$ and $\Theta_D = 340$ K. These values are compared with $\gamma = 11 \text{ mJ}/(\text{K}^2 \cdot \text{mol})$ and $\Theta_D = 345$ K for the polycrystalline sample [8].

Next, we show in Fig. 1(c) the temperature dependence of the magnetic susceptibility $\chi$ for three principal directions, [100], [110], and [111] in CoSe$_2$. The magnetic susceptibility increases with decreasing temperature, possesses a broad peak at around 50 K and becomes approximately constant below 15 K. Anisotropy of the susceptibility was not observed among the three directions. Note that the Curie–Weiss law with the effective magnetic moment $\mu_{\text{eff}} = 1.72 \mu_B$/Co is observed above 300 K [3], as mentioned in Introduction.
Similarly, we measured the electrical resistivity, specific heat, and magnetization $M$ in the ferromagnet CoS$_2$, as shown in Fig. 1. The ferromagnetic ordering at $T_C = 122$ K is the first-order-like phase transition, revealing sharp peaks in the resistivity and specific heat, as shown in Figs. 1(a) and 1(b). The $\rho_0$ and RRR are $\rho_0 = 0.42 \ \mu\Omega\cdot$cm and RRR = 410, revealing a high-quality sample. The $\gamma = 21$ mJ/(K$^2$-mol) is slightly larger than 18 mJ/(K$^2$-mol) in CoSe$_2$. Note that the previous $\gamma$ values in CoS$_2$ are 25.8 mJ/(K$^2$-mol) [4] and 21.6 mJ/(K$^2$-mol) [9] for the single crystal samples. The ordered moment $s$ is $s = 0.93 \ \mu_B$/Co at 2 K, as shown in Fig. 1(c). Note that the saturated moments at 2 K are 0.933 $\mu_B$/Co for $H \parallel [110]$ and 0.928 $\mu_B$/Co for $H \parallel [100]$ and [111], revealing a small difference of 0.005 $\mu_B$/Co between $H \parallel [110]$ and $H \parallel [100]$ and [111]. These values are slightly larger than the previous values of 0.89 $\mu_B$/Co for $H \parallel [100]$ and [111] in the magnetization curve at 4.2 K [4], but are close to 0.91 $\mu_B$/Co in the magnetization curve at 5 K [10] and 0.92(4) $\mu_B$/Co obtained from the polarized neutron scattering experiment at 1.8 K [11]. These cited values were obtained for single crystal samples, which are larger than the value of 0.85 $\mu_B$/Co for the polycrystalline sample mentioned in Introduction [3].

Next, we carried out the dHvA experiment for CoSe$_2$ and CoS$_2$. Figures 2(a) and 2(b) show the typical dHvA oscillations for $H \parallel [111]$ and the corresponding fast Fourier transformation (FFT) spectrum, respectively, for CoSe$_2$. Four dHvA branches named $\beta$, $\gamma$, $\varepsilon_{1,2}$, and $\delta$ branches are observed. The dHvA frequency $F$ is in the range from $0.548 \times 10^7$ to $2.517 \times 10^7$ Oe. Here, the dHvA frequency $F = c h S_F/2 \pi e$ is proportional to the maximum or minimum cross-sectional area of the Fermi surface $S_F$, which is shown as a unit of magnetic field. We determined the cyclotron masses $m_c^*$ for these branches from the temperature dependences of the dHvA amplitudes. The cyclotron mass, which is described in Fig. 2(b), is in the range from 0.9 to
Figure 2. (Color online) (a) Typical dHvA oscillations and (b) the corresponding FFT spectrum for $H \parallel [111]$, and (c) theoretical Fermi surfaces in CoSe$_2$. Figures in parentheses are cyclotron effective masses for dHvA branches.

The Fermi surfaces consist of band 93rd and 94th hole Fermi surfaces and the compensated band 95th and 96th electron Fermi surfaces. Note that the unit cell contains four molecules of CoSe$_2$ and then electrons are even in number, meaning equal volumes of the hole and electron Fermi surfaces. The detected dHvA branches are identified from the results of band calculations, as follows: (1) branch $\beta$ is due to a nearly spherical band 95th electron Fermi surface centered at the R point, (2) branch $\gamma$ is due to a nearly spherical band 96th electron Fermi surface centered at the R point, (3) branches $\epsilon_i$ ($i = 1, 2, 3$) are due to nearly spherical band 93rd hole Fermi surfaces centered at the M point.
Figure 3. (Color online) (a) Typical dHvA oscillations and (b) the corresponding FFT spectrum, and (c) theoretical Fermi surfaces in CoS$_2$. Figures in (b) correspond to the cyclotron effective masses, for example $13m_0$ for branch $\alpha$.

branch $\delta$ is due to a spherical band 96th electron Fermi surface centered at the $\Gamma$ point, although the theoretical Fermi surface is larger than the experimental one in volume, and (5) theoretically, much larger Fermi surfaces exist, which are due to a nearly spherical band 95th electron Fermi surface named $\alpha$ and a multiply-connected band 94th hole Fermi surfaces with vacant space in center. These branches were not observed experimentally mainly because of large cyclotron masses of ($10$–$20m_0$) and a quality of the sample (RRR = 49).

We show later in Fig. 4(a) the total and partial densities of states in CoSe$_2$. As discussed in Introduction, the bonding $e_g$ band spreads widely in the energy range from 0 to 0.35 Ry, the $t_{2g}$ band forms a very narrow band around 0.40–0.45 Ry, and the antibonding $e_g$ band spreads from 0.5 to 0.7 Ry in energy. All these bands are formed mainly from contributions of Co-3$d$ and Se-4$p$ electrons. A dominant contribution is due to Co-3$d$ electrons. A quarter-filled $e_g$ band is characteristic in the density of states, revealing a large density of states at Fermi energy in a narrow band. The theoretical $\gamma_h$ value is $\gamma_h = 6.93$ mJ/(K$^2$·mol). The experimental $\gamma$ value of 18 mJ/(K$^2$·mol) is by 2.6 times larger than the theoretical one.

Similarly, we carried out the dHvA experiments for the ferromagnet CoS$_2$. Figures 3(a) and 3(b) show the typical dHvA oscillations in the ferromagnetic state of CoS$_2$ and the corresponding FFT spectrum, respectively. A main dHvA branch named $\alpha$ possesses a dHvA frequency of $6.506 \times 10^7$ Oe. The cyclotron effective mass is unexpectedly large, $13m_0$. The other branches are also large, ranging from 2.6 to $19m_0$. 
Figure 3(c) shows the theoretical Fermi surfaces. Here, the present band calculations were carried out using the FLAPW method within the local spin density approximation where the ferromagnetic state is assumed, but the spin-orbit interaction is neglected for simplicity. The lattice parameters are adopted from ref. [13], namely $a = 5.5385$ Å and $x = 0.38988$ for S. 3$p^3$3$d^7$4$s^2$ electrons for Co and 3$s^2$3$p^4$ electrons for S are treated as valence electrons.

It is characteristic that Fermi surfaces are constructed only from the spin-up band. The Fermi energy is located just below the antibonding $e_g$ band with the spin-down state, revealing a half-metallic spin state. The Fermi surfaces in Fig. 3(c) is thus based on the 56th hole spin-up band and the compensated 57th electron spin-up and 58th electron spin-up bands. Note that the theoretical dHvA frequency of branch $\alpha$ for $H \parallel [001]$ is $F_b = 6.352 \times 10^7$ Oe, which is close to the experimental value of $F = 6.506 \times 10^7$ Oe, while the corresponding band mass of $m_b = 0.68m_0$ is compared with the experimental value of $m_c^* = 13m_0$. Theoretically, Co-$3d$ electrons produce a magnetic moment of 0.88 $\mu_B$/Co.

4. Concluding Remark
Finally, we discuss the ferromagnetic ordering and the Fermi surface properties in CoS$_2$. Figures 4(a), 4(b), 4(c), and 4(d) show the total and partial densities of states in CoSe$_2$, the Co-$3d$ partial density of states in the paramagnetic state of CoS$_2$, and the Co-$3d$ partial densities of states in the ferromagnetic spin-up and -down states of CoS$_2$, respectively. Note that the Co-$3d$ partial density of states is roughly the same between CoS$_2$ and CoSe$_2$ in the paramagnetic state. Correspondingly, the theoretical $\gamma_b$ value of 6.62 mJ/(K$^2$·mol) in the paramagnetic state of CoS$_2$ is approximately the same as $\gamma_b = 6.93$ mJ/(K$^2$·mol) in CoSe$_2$. Important is that the band width below the Fermi energy in the paramagnetic state of CoS$_2$ is much narrower than that in CoSe$_2$. Moreover, there exists a much larger Co-$3d$ partial density of states below the Fermi energy in the paramagnetic state of CoS$_2$, which produces a ferromagnetic ordering at low temperatures in CoS$_2$. Note that the theoretical $\gamma_b$ value in the ferromagnetic state is 3.03 mJ/(K$^2$·mol), which is smaller than $\gamma_b = 6.62$ mJ/(K$^2$·mol) in the paramagnetic state. The present small theoretical value of $\gamma_b = 3.03$ mJ/(K$^2$·mol) in the ferromagnetic state is compared with the experimental value of $\gamma = 21$ mJ/(K$^2$·mol), revealing a large enhancement of the $\gamma$ value, $\gamma/\gamma_b = 7$. From these experimental results, an electronic state of CoS$_2$ is close to a quantum critical point, which is defined as an electronic state of $T_C \rightarrow 0$. In fact, the Curie temperature becomes zero in Co(S$_{1-x}$Se$_x$)$_2$ with $x = 0.11$ [14].

Moreover, as shown in Fig. 4(c), only the spin-up state in the $e_g$ band is occupied by the Co-$3d$ electrons, while the spin-down state is empty, revealing the half-metallic spin state. This is a main reason why the large ordered moment of $\mu_b = 0.93 \mu_B$/Co is realized in CoS$_2$. It is thus concluded that a large ordered moment, together with a large $\gamma$ value, is a characteristic feature in CoS$_2$.

Acknowledgments
We are very grateful to Prof. K. Ueda for helpful discussions. This work was supported by JSPS KAKENHI Grant Numbers 15H05884, 25247055, and 15H05886.

References
[1] Sidorov V A, Krasnorussky V N, Petrova A E, Utyuzh A N, Yuhasz W M, Lograsso T A, Thompson J D and Stishov S M 2011 Phys. Rev. B 83 060412
[2] Leighton C, Manno M, Cady A, Freeland J W, Wang L, Umemoto K, Wentzcovitch R M, Chen T Y, Chien C L, Kuhns P L, Hoch M J R, Reyes A P, Moulton W G, Dahlberg E D, Chechelsky J and Eckert J 2007 J. Phys.: Condens. Matter 19 315219
[3] Adachi K, Sato K and Takeda M 1969 J. Phys. Soc. Jpn. 26 631
[4] Hiraka H and Endoh Y 1994 J. Phys. Soc. Jpn. 63 4573
Figure 4. (Color online) Total and partial densities of states in (a) the paramagnetic CoSe$_2$, (b) Co-3$d$ partial densities of states in the paramagnetic CoS$_2$, and (c) and (d) the ferromagnetic CoS$_2$.

[5] Ishiguro A, Sawada A, Suzuki M, Hiraka H, Yamada K, Endoh Y and Komatsubara T 1998 J. Magn. Magn. Mater. 177–181 1355
[6] Moriya T 1985 Spin Fluctuations in Itinerant Electron Magnetism (Berlin Heidelberg: Springer-Verlag) p 152
[7] Wang L, Chen T Y, Chien C L and Leighton C 2006 Appl. Phys. Lett. 88 232509
[8] Ogawa S and Nishihara Y 1977 J. Phys. Soc. Jpn. 42 343
[9] Otero-Leal M, Rivadulla F, García-Hernández M, Piñeiro A, Pardo V, Baldomir D and Rivas J 2008 Phys. Rev. B 78 180415
[10] Yamamoto R, Machida A, Moritomo Y and Nakamura A 1999 Phys. Rev. B 59 R7793
[11] Brown P J, Neumann K-U, Simon A, Ueno F and Ziebeck K R A 2005 J. Phys.: Condens. Matter 17 1583
[12] Furuseth S, Kjekshus A and Andresen A F 1969 Acta Chem. Scand. 23 2325
[13] Nowack E, Schwarzenbach D and Hahn T 1991 Acta Crystallogr. B 47 650
[14] Goto T, Shindo Y, Takahashi H and Ogawa S 1997 Phys. Rev. B 56 14019