Abstract. We report the synthesis and basic properties of the binary compound Yb$_5$Si$_4$. In this compound, Yb ions occupy three different crystallographic sites, the multiplicity of which is represented by Yb$_1$ : Yb$_2$ : Yb$_3$ = 1 : 2 : 2. The estimated effective magnetic moment and magnetic entropy can be explained by the proportion of Yb valence states, Yb$^{3+}$ : Yb$^{2+}$ = 2 : 3. This result suggests the possibility that Yb$^{3+}$ ions occupy either Yb$_2$ or Yb$_3$ site. Yb$_5$Si$_4$ undergoes an antiferromagnetic transition at $T_N$ = 1.7 K. The extended high temperature tail in the temperature dependence of the specific heat just above $T_N$ has been observed. Yb$_5$Si$_4$ also exhibits the broad maximum peak around 2.3 K in the magnetic susceptibility, corresponding to the specific heat anomaly. We propose that these anomalies are possible to originate from magnetic fluctuations caused by low-dimensional Yb$^{3+}$ networks. Electrical resistivity measurements on Yb$_5$Si$_4$ reveal semiconducting behavior at all temperatures. The small energy gap $\Delta$ = 430 K has been obtained at room temperature estimated by the thermal activation model. The energy gap gradually decreases with decreasing temperature, and reaches about 3 K at low temperatures.

1. Introduction
Yb-based intermetallic compounds are attractive with respect to their interesting physical properties. Recently, anomalous magnetism based on low-dimensional magnetic fluctuations have been reported. Yb$_2$Pt$_2$Pb [1] and YbNiB$_4$ [2] exhibit a broad maximum in the temperature dependence of the magnetic susceptibility above an antiferromagnetic ordering temperature. Specific heat measurements display a shoulder-type anomaly in the same temperature range for which the susceptibility anomaly occurs. These features are considered to be due to low-dimensional magnetic fluctuations, which arise from their characteristic crystal structures. Both compounds possess a clear layered structure, Yb$_2$Pt$_2$Pb includes the Shastry-Sutherland network of Yb$^{3+}$ ions. YbAl$_3$C$_3$, having the two-dimensional triangular lattice of Yb$^{3+}$ ions, exhibits the spin-gap state because of forming the spin dimer [3, 4]. The development of the spin-gap below 9 K, observed by inelastic neutron measurement, rapidly reduces the magnetic susceptibility, and then a broad maximum occurs around 9 K in the $\chi$ − $T$ curve.

Furthermore, the valence instability of Yb ions affects physical properties on Yb-based compounds. The valence state of Yb ion is varied between nonmagnetic Yb$^{2+}$ (4f$^{14}$) state and Yb$^{3+}$ (4f$^{13}$) state by its surroundings in the crystal structure. Yb$_4$As$_3$ shows a charge ordering,
from the mixed valence state at the high-temperature phase, accompanied by a structural phase transition at 290 K [5], below which \(\text{Yb}^{3+}\) ions are aligned along the [111] direction [6]. The charge ordering causes the one-dimensional chains of \(\text{Yb}^{3+}\) ions, therefore \(\text{Yb}_4\text{As}_3\) exhibits one-dimensional magnetism, which was demonstrated by the observation of the dispersion relation anticipated in the model of one-dimensional spin \(\frac{1}{2}\) Heisenberg antiferromagnet using inelastic neutron measurements [7, 8].

\(\text{Yb}_5\text{Si}_4\), the subject material in the study, crystallizes in the orthorhombic structure belonging to the space group of \(Pnma\). The crystal structure type of \(\text{Yb}_5\text{Si}_4\), there were two candidates [9, 10], has been determined to be \(\text{Gd}_5\text{Si}_4\)-type by Ahn et al. [11]. The magnetic properties were reported by Ahn et al. [11] and Dhar et al. [12]. Ahn suggested that Yb atoms can exist in two valence states, \(\text{Yb}^{3+}\) or \(\text{Yb}^{2+}\). The fraction of \(\text{Yb}^{3+}\) ions in the unit cell was evaluated to be 0.39 from the interpretation of the estimated effective magnetic moment. On the other hand, Dhar investigated the valence state of Yb ions using Mössbauer spectroscopy measurements. They claimed that 1/3 of the Yb ions are trivalent and undergo magnetic ordering while the remaining 2/3 possess a valency slightly deviating from 3 because of a strong \(c-f\) hybridization effect, the latter Yb ions do not participate in the magnetic ordering at low temperatures. In addition to this, there is a disagreement with the magnetic transition temperature reported in these two literatures. An antiferromagnetic ordering occurs at 2.4 K suggested by Ahn et al., on the other hand, a magnetically ordered state is realized below 1.65 K indicated by Dhar et al. It is the purpose of this paper to settle this conflict and discuss the physical properties of \(\text{Yb}_5\text{Si}_4\).

2. Experimental
Polycrystalline samples of \(\text{Yb}_5\text{Si}_4\) were prepared by induction melting of the stoichiometric amounts of the constituent elements, ytterbium pieces (99.9%) and silicon pieces (99.999%). The elements were placed in an encapsulated molybdenum crucible. In attempt to prevent the attack against the inner wall of the molybdenum crucible by silicon, we inserted a tantalum container, the thickness and the length of which are 1 mm and 20 mm, into the crucible. The crucible is slowly heated up to 1700 °C using a high-frequency induction furnace, since the melting point of \(\text{Yb}_5\text{Si}_4\) was reported to be about 1680 °C [9, 13, 14], and then slowly cooled. The purity of the obtained polycrystalline samples was confirmed by X-ray powder diffraction using Cu-K\(\alpha\) radiation. The X-ray diffraction pattern exhibits only the characteristic lines of the \(\text{Gd}_5\text{Si}_4\)-type structure with the space group of \(Pnma\) [11].

Magnetic measurements were performed in the temperature range of 1.8 – 300 K and in applied magnetic fields up to 7 T using a SQUID magnetometer (Quantum Design, MPMS XL-7). Specific heat and electrical resistivity were measured in the temperature range of 0.4 – 300 K by a conventional relaxation method and a standard four-probe method using PPMS (Quantum Design).

We used shaped polycrystalline samples for specific heat and electrical resistivity measurements. For magnetization measurements, oriented powder samples were also used in addition to normal polycrystalline samples. When bulk samples were employed for measurements, it was difficult to reproduce the absolute value of the magnetization. For this reason, there seems to be a direction dependence in spite of the polycrystalline sample, presumably due to the possession of easy direction for crystal growth. Accordingly, powdered samples which were oriented by applying magnetic fields of up to 7 T at \(T = 1.8\) K were used for magnetization measurements, in order to obtain reproducible data and information about the easy direction magnetization.
3. Results and discussion

The temperature dependence of the magnetic susceptibility is shown in Fig. 1. The oriented powder sample, as mentioned in the experimental section, was used for this measurement. A broad peak anomaly, the top of which is $T_{\text{max}} = 2.3$ K, has been observed in a magnetic field of 0.1 T. This anomaly is essentially the same as that previously reported by Ahn et al. [11]. They described the anomaly as the indication of an antiferromagnetic ordering. However, our specific measurements, as described later, a long-range magnetic ordering occurs at $T_N = 1.7$ K. We conclude that the origin of this broad peak anomaly is not due to the antiferromagnetic ordering. The anomaly shifts toward lower temperatures and is suppressed with increasing magnetic field. The inset shows the temperature variation of the inverse magnetic susceptibility of Yb$_5$Si$_4$ using the normal polycrystalline sample. The magnetic susceptibility satisfies a Curie-Weiss law above 100 K, with the effective magnetic moment $\mu_{\text{eff}} = 2.92$ $\mu_B$ and the paramagnetic Curie temperature $\theta_P = -14$ K. These values are in good agreement with the previous reported value, $\mu_{\text{eff}} = 2.84$ $\mu_B$ and $\theta_P = -16$ K [11]. Considering the reasonable ratio of Yb$^{3+}$ and Yb$^{2+}$ from the value of the effective magnetic moment, it is estimated to be almost Yb$^{3+}$ : Yb$^{2+} = 2 : 3$ using the following equation:

$$\mu_{\text{eff}} = \left\{ n^{3+}(\mu^{3+})^2 + (1 - n^{3+})(\mu^{2+})^2 \right\}^{\frac{1}{2}}, \quad (1)$$

where $\mu^{3+}$ and $\mu^{2+}$ are the theoretical free magnetic moments of each valence state (4.54 $\mu_B$ and 0 $\mu_B$, respectively), and $n^{3+}$ is the fraction of Yb sites occupied by the magnetic Yb$^{3+}$ ion. In the crystal structure of Yb$_5$Si$_4$, there are a total of 20 Yb atoms per unit cell distributed among three crystallographic sites, the multiplicity of which is Yb1(4c) : Yb2(8d) : Yb3(8d) = 4 : 8 : 8. This ratio can be reduced to 1 : 2 : 2. Assuming that 2 of 5 Yb atoms per mol Yb$_5$Si$_4$ are in the Yb$^{3+}$ state, and the remaining 3 are in the Yb$^{2+}$ state, our analysis can be explained and is

![Figure 1](image1.png)

Figure 1. Low-temperature magnetic susceptibilities of Yb$_5$Si$_4$ as a function of temperature at various magnetic fields. The inset shows the temperature dependence of the reciprocal magnetic susceptibility at $\mu_0H = 0.1$ T.

![Figure 2](image2.png)

Figure 2. Isothermal magnetization curves of Yb$_5$Si$_4$ at various temperatures. The inset shows the derivatives of the magnetization with respect to the magnetic field at $T = 1.8$ and 4 K.
consistent with the previously reported fraction of Yb$^{3+}$ ions, the value of which was estimated to be $0.39 \approx 2/5$ [11]. This result suggests the possibility that Yb$^{3+}$ ions occupy either Yb2 or Yb3 site.

The magnetization curves of Yb$_5$Si$_4$ at various temperatures are shown in Fig. 2. To obtain information about the easy direction magnetization, the oriented powder samples were employed. At the lowest temperature of 1.8 K, the saturation magnetization is estimated to be 0.94 $\mu_B$ at $\mu_0 H = 7$ T. This value is approximately the same magnitude published in the literature [11]. This value is converted into 2.35 $\mu_B$ per Yb$^{3+}$ ion, significantly reduced from the theoretical $g_J J$ maximal value of 4.0 $\mu_B$, where $g_J$ is the Landé $g$-factor, and is most likely due to crystal-field splitting. Furthermore, the metamagnetic-like behavior, which was also indicated in Ref. [11], has been observed around $\mu_0 H = 1.2$ T at $T = 1.8$ K. The transition behavior can be seen more clearly by taking a field derivative of the magnetization as shown in the inset. The anomaly disappears at 4 K, corresponding to the temperature above $T_{\text{max}}$ defined from the $\chi - T$ curve. This metamagnetic-like behavior seems to appear below the characteristic temperature $T_{\text{max}}$.

We have performed specific heat measurements on Yb$_5$Si$_4$ down to 0.4 K, the first report of measurements below 1.8 K. Figure 3(a) shows the temperature variation of the specific heat of Yb$_5$Si$_4$. A lambda-type anomaly is clearly observed at 1.7 K, indicating a long-range magnetic
ordering. This interpretation is consistent with the observation of large splitting on Mössbauer spectra at 1.5 K and 80 mK [12]. The magnetic ordering is expected to be an antiferromagnetic one since an antiferromagnetic correlation exists in the paramagnetic region indicated from the sign of $\theta_p$. Furthermore, the $C - T$ curve displays a shoulder-type anomaly above $T_N = 1.7$ K. This anomaly corresponds to the broad peak found in the magnetic susceptibility around $T_{\text{max}}$.

The magnetic entropy $S_{\text{mag}}$ is presented in Fig. 3(b). We obtained the magnetic contribution to the specific heat by subtracting the phonon contribution, which was estimated by fitting the data up to room temperature using the Debye function ($\Theta_D = 217$ K). The estimated phonon contribution is quite small below 10 K, compared to the experimental values. The evaluated $S_{\text{mag}}$ reaches $2/5$ of $R \ln 2$ per Yb mole of Yb$_3$Si$_4$ around 10 K. Here, let us examine the $S_{\text{mag}}$ using the analogous method when we applied it to the analysis of the value of the effective magnetic moment. The ratio of $2/5$ is equivalent to the fraction of Yb$^{3+}$ state in the unit cell. This result implies that the $S_{\text{mag}}$ reaches $R \ln 2$ per Yb$^{3+}$ ion around 10 K. Accordingly, the crystalline electric field (CEF) ground state of Yb$^{3+}$ ions can be considered as a Kramers doublet. The $S_{\text{mag}}$ at $T_N$, however, reduces from the value $2/5$ $R \ln 2$ expected for the Kramers doublet of the Yb$^{3+}$ ion in the unit cell. This is considered to originate from the existence of magnetic fluctuations above $T_N$. Yb$^{3+}$ ions are possible to occupy either Yb2(8d) or Yb3(8d) site, as mentioned above. In either case, this should lead to the establishment of low-dimensional networks of magnetic Yb$^{3+}$ ions, producing low-dimensional magnetic fluctuations. For the Sommerfeld coefficient of the electronic specific heat $\gamma$, it is difficult to estimate it because the antiferromagnetic transition occurs at low temperatures ($T_N = 1.7$ K). The $\gamma$ is roughly determined to be 220 mJ/Yb mol K$^2$.

Figure 4 shows the temperature dependence of the electrical resistivity of Yb$_3$Si$_4$. The resistivity $\rho$ indicates the large value of 0.2 $\Omega$·cm at room temperature and then reveals a semiconducting increase with decreasing temperature, and finally reaches 2.2 $\Omega$·cm at $T = 0.5$ K. To evaluate the energy gaps with a thermal activation function of $\rho = \rho_0 \exp(\Delta/2k_B T)$, the Arrhenius plot is displayed as shown in the inset of Fig. 4. Slopes of the dotted lines above 160 K and below 10 K give energy gap values of $\Delta_1 = 430$ K and $\Delta_2 = 3.3$ K. The gap gradually decreases with decreasing temperature from room temperature, and then drastically changes around 50 K. This behavior is similar to that of Kondo semiconductor Ce$_3$Bi$_4$Pt$_3$ [15]. In addition to these results, the large Sommerfeld coefficient $\gamma$ suggests the possibility of categorizing Yb$_3$Si$_4$ as a Kondo semiconductor. However, the magnetic susceptibility does not show an obvious corresponding anomaly around 50 K. At this stage, it can not be concluded that the drastic change in the gap structure is caused by the Kondo effect. The CEF effect, observed as the deviation from the Curie-Weiss behavior blow 50 K in the reciprocal magnetic susceptibility, may be associated with suppressing the gap formation. Further investigation is necessary to resolve this issue.

4. Conclusion
We have been revealed that Yb$_3$Si$_4$ shows the antiferromagnetic transition at $T_N = 1.7$ K. Evidence of magnetic fluctuations is found in the magnetic susceptibility, which has the broad peak above $T_N$, and in the suppression of the magnetic entropy at $T_N$. The analogous features were observed in Yb$_2$Pt$_3$Pb [1] and YbNIB$_4$ [2], having the low-dimensional and localized moment systems. The magnetic fluctuations in Yb$_3$Si$_4$ are also attributed to the low-dimensional magnetism, which should be brought about by networks of magnetic Yb$^{3+}$ ions occupying one crystallographic site out of three Yb sites. Electrical resistivity indicates semiconducting behavior with the small energy gap, which is reducing with decreasing temperature, as observed in Kondo semiconductors.
Acknowledgments
This work was supported by a Grant-in-Aid for Research (No. 24540359) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References
[1] Kim M S, Bennett M C and Aronson M C 2008 Phys. Rev. B 77 144425
[2] Prasad A, Hossain Z, Jeevan H S and Geibel C 2009 J. Phys.: Condens. Matter 21 206003
[3] Ochiai A, Inukai T, Matsumura T, Oyamada A and Katoh K 2007 J. Phys. Soc. Jpn 76 123703
[4] Kato Y, Kosaka M, Nowatari H, Saiga Y, Yamada A, Kobyama T, Katano S, Ohoyama K, Suzuki H S, Aso N and Iwasa K 2008 J. Phys. Soc. Jpn. 77 053701
[5] Ochiai A, Suzuki T and Kasuya T 1990 J. Phys. Soc. Jpn. 59 4129
[6] Goto T, Nemoto Y, Ochiai A and Suzuki T 1999 Phys. Rev. B 59 269
[7] Kohgi M, Iwasa K, Mignot J M, Ochiai A and Suzuki T 1997 Phys. Rev. B 56 R11388
[8] Kohgi M, Iwasa K, Mignot J M, Gukasov A, Fak B, Hiess A, Ochiai A and Aoki H 2002 Appl. Phys. A 74 S871
[9] Palenzona A, Manfrinetti P, Brutti S and Balducci G 2003 J. Alloys Compd. 348 100
[10] Černý R and Alami-Yadri K 2003 Acta Crystallogr. Sect. E: Struct. Rep. Online 59 i1
[11] Ahn K, Tsokol A O, Mozharivskýj Y, Gschneidner K A and Pecharsky V K 2005 Phys. Rev. B 72 054404
[12] Dhar S K, Manfrinetti P, Palenzona A and Bonville P 2003 Acta Phys. Pol., B 34 1461
[13] Bruttì S, Balducci G, Ciccioli A, Gigli G, Manfrinetti P and Palenzona A 2003 Intermetallics 11 1153
[14] Bruttì S, Balducci G, Ciccioli A and Gigli G 2005 Calphad 29 254
[15] Cooley J C, Aronson M C and Canfield P C 1997 Phys. Rev. B 55 7533