Magnetic Properties and Specific Heat of Ce₃Pb₃ Compound

K. Sasao, R. Yamauchi and K. Fukamichi
Department of Materials Science, Graduate School of Engineering,
Tohoku University, Aoba-yama 02, Sendai 980-8570, Japan

(Received; May 6, 1998, Accepted; August 26, 1998)

Magnetic and specific heat measurements of Ce₃Pb₃ compound with a Mn₃Si₃-type structure have been carried out. The magnetic susceptibility shows two peaks at 3.5 and 20.5 K due to the magnetic transitions. The paramagnetic Curie temperature and the effective magnetic moment obtained from the magnetic susceptibility are −8.2 K and 2.6μB, respectively. These results indicate that 4f electrons are localized in high temperatures and the ground state is antiferromagnetic. The electronic specific heat coefficient, γ, is about 120 mJ/°C-mol K², and the Debye temperature, θ_D, is estimated to be 150 K. From these results, it is concluded that Ce₃Pb₃ is an antiferromagnetic heavy-fermion compound. The Néel temperature T_N of Ce₃Pb₃ compound is higher than that of other Ce-Pb compounds, which is related to the two kinds of Ce sites.

Key words: Ce₃Pb₃, antiferromagnetic, heavy fermion, Mn₃Si₃-type structure, magnetic susceptibility, specific heat

1. Introduction

Many of Ce and U compounds which have a very large electron mass due to the highly electron correlations are generally called heavy fermion compounds. Recently, heavy fermion compounds have been investigated extensively, because these compounds show various ground states such as nonmagnetic, antiferromagnetic or superconductivity. The properties in the ground state of heavy fermion compounds are closely connected with the RKKY interaction and the Kondo temperature. Doniach ³ has proposed a model that the Néel temperature T_N depends on the ratio between the exchange coupling constant J and the conduction-electron bandwidth W for the antiferromagnetic heavy fermion compounds.

Although the phase diagram of Ce-Pb system is incomplete, five phases have been reported until now. Among them, CePb₃ and CePb₂ are well known as antiferromagnetic heavy fermion compounds, competing between the RKKY interaction and the Kondo effect. However, the magnetic properties of other compounds for Ce-Pb system have not been investigated yet. Ce₃Pb₃ compound has a Mn₃Si₃-type structure and there is two kinds of Ce sites in the unit cell. Most of studies about the heavy fermion compounds are made for the Ce system compounds which have one equivalent Ce site. It is interesting to investigate the magnetic and heavy fermion characteristics of Ce-rich compounds having two kinds of Ce sites.

We have made the magnetic and specific heat measurements to investigate the magnetic and heavy fermion characteristics of Ce₃Pb₃ compound. Furthermore, we compare the magnitude of the Néel temperature T_N with that of other Ce-Pb compounds.

2. Experimental

The starting materials were Ce of 99.9% and Pb of 99.99% purities. The specimens were prepared by arc melting in an argon gas atmosphere. The buttons were remelted 4 times in order to ensure good homogeneity. The specimen was annealed at 873 K for 24 hours in an evacuated quartz tube.

During the powder X-ray diffraction measurement, the powder sample was protected by 2-propanol, because Ce₃Pb₃ easily reacts with humidity.

The magnetization up to 55 kOe and the temperature dependence of DC magnetic susceptibility from 1.8 to 300 K were measured with a SQUID magnetometer. The specific heat measurement from 1.8 to 60 K was made by a relaxation heat capacity method.

3. Results and discussion

A single phase of Ce₃Pb₃ compound was identified by the powder X-ray diffraction analysis. Figure 1 shows the temperature dependence of the magnetic susceptibility and its inverse measured at 10 kOE magnetic field in the temperature range from 1.8 K to 150 K. The dashed line represents the Curie-Weiss law, being accordant with the experimental result at higher temperatures. The paramagnetic Curie temperature is −8.2 K. The effective magnetic moment is 2.6μB, close to the theoretical value of Ce³⁺. Consequently, 4f electrons in Ce₃Pb₃ compound are localized at higher temperatures. In low temperatures, on the other hand, the magnetic susceptibility exhibits two peaks at 3.5 and 20.5 K due to the magnetic transitions.

Figure 2(a) displays the magnetization, M up to 55 kOe at 1.8, 15 and 25 K. The differential magnetization dM/dH as a function of temperature is shown Fig. 2(b). The magnetization at 25 K linearly increases against applied magnetic field, showing a paramagnetic property. In contrast, dM/dH at 1.8 K changes remarkably around at 3 and 30 kOe, and a sluggish change around at 30 kOe occurs at 15 K. From these
Fig. 1. Temperature dependence of the magnetic susceptibility $\chi$ and its inverse $1/\chi$ measured in a field of 10 kOe. The dashed line stands for the Curie-Weiss law.

Fig. 2. (a) Magnetization curves at 1.8, 15 and 25 K. (b) Differential magnetization curves as a function of temperature.

Fig. 3. Temperature dependence of the total specific heat divided by the temperature. The dashed line represents $\gamma + C_{ph}/T$.

results, the ground state of this compound is antiferromagnetic. Moreover, a magnetic order-order transition may occur at 3.5 K, because the behavior of the magnetization at 1.8 K and 15 K is different. Such plural magnetic transitions are observed among Ce compounds having two or more different Ce sites in their crystalline structure. The curvature of the magnetization at 1.8 K in Fig. 2(a) would be caused by the change of the magnetic state from the applied magnetic field or by the magnetocrystalline anisotropy.

The specific heat in the form of $C_{total}/T - T$ given in Fig. 3. Generally, the total specific heat $C_{total}$ is given by the following expression:

$$C_{total}/T = \gamma + C_{mag}/T + C_{ph}/T,$$

where $\gamma$ is the electronic specific heat coefficient, $C_{mag}$ the magnetic contribution to the specific heat and $C_{ph}$ the lattice specific heat, which follows Debye’s $T^3$ law at lower temperatures. In this discussion, we obtain $C_{ph}$ by calculating the Debye function

$$C_{ph} = 9N_Ak_B\left(\frac{T}{\theta_D}\right)^3 \int_0^{\frac{T}{\theta_D}} \frac{z^4e^z}{(e^z-1)^2}dz,$$  

where $N_A$ is the Avogadoro number, $k_B$ the Boltzmann constant, $\theta_D$ the Debye temperature. In this figure, a dashed line represents $\gamma + C_{ph}/T$. From these discussion mentioned above, $\gamma$ and $\theta_D$ is about 120 mJ/deg-K$^2$ and 150 K, respectively. Two peaks are also observed in Fig. 3 and their temperatures are agree with the data of the magnetic measurements. The entropy of $C_{mag}$ defined as the difference between $C_{total}$ and $\gamma T + C_{ph}$ reaches 0.6 Kln2 at 20.5 K. The reduction of the entropy from the theoretical value is due to itinerant-character of $4f$ electrons, and this behavior is characteristic of heavy fermion compounds. From the present results of the magnetic and specific heat.
Table 1. The Néel temperatures $T_N$ and the electronic specific heat coefficients $\gamma$ for Ce$_5$Pb$_3$, CePb$_2$ and CePb$_3$ compounds.

<table>
<thead>
<tr>
<th></th>
<th>Ce</th>
<th>$T_N$ [K]</th>
<th>$\gamma$ [mJ/mol K$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce$_5$Pb$_3$</td>
<td>62.5</td>
<td>20.5</td>
<td>$\sim$120</td>
</tr>
<tr>
<td>CePb$_2$</td>
<td>33.3</td>
<td>3.6</td>
<td>$^{(a)}$210 $^{(a)}$</td>
</tr>
<tr>
<td>CePb$_3$</td>
<td>25.0</td>
<td>1.16</td>
<td>$^{(b)}$250 $^{(c)}$</td>
</tr>
</tbody>
</table>

$^{(a)}$ Hattori et al. (1994).  $^{(b)}$ Vettier et al. (1986)  $^{(c)}$ Pillmayr et al. (1990)

measurements, it is confirmed that Ce$_5$Pb$_3$ is an antiferromagnetic heavy fermion compound.

The Néel temperature $T_N$ and the $\gamma$-value of Ce$_5$Pb$_3$, CePb$_2$ and CePb$_3$ are listed in Table 1, for comparison. With increasing the Ce content, $T_N$ increases and the $\gamma$-value decreases. In these compounds, the competition between the RKKY interaction and the Kondo effect results in an antiferromagnetic ordering and a heavy fermion characteristics. The RKKY interaction and the Kondo effect are antipodal characters, and it has been thought that the magnitude of $T_N$ is decided by their valance $^{3)}$. It should be note that $T_N$ of Ce$_5$Pb$_3$ is high in spite of the large $\gamma$-value. In the case of CePb$_3$ compound with one equivalent Ce site, it has been reported from neutron diffraction measurement that the ordered moment is smaller than the theoretical value because of itinerant-character of 4$f$ electrons $^{6)}$. On the other hand, Lawrence et al. reported the magnetic ordering at 17.5 K of Ce$_5$Sn$_3$ compound with two kinds of Ce sites does on the higher-symmetry Ce site and the heavy fermion behavior does on the lower-symmetry site $^{10)}$. Taking into consideration Ce$_5$Pb$_3$ has also two kinds of Ce sites, such a high $T_N$ would be caused by either of two Ce sites which have a localized-character.

4. Conclusion

The magnetic and specific heat measurements of Ce$_5$Pb$_3$ compound have been made in order to investigate the magnetic and heavy fermion properties. The main results are summarized as follows.

(a) Temperature dependence of the magnetic susceptibility follows the Curie-Weiss law in high temperature regions. The paramagnetic Curie temperature is $-8.2$ K and the effective magnetic moment is $2.6\mu_B$, indicating that 4$f$ electrons are localized in higher temperatures.

(b) The magnetic and specific heat data show that the ground state is antiferromagnetic, and an order-order magnetic transition occurs below the Néel temperature.

(c) The electronic specific heat coefficient is about 120 mJ/mol K$^2$. The entropy of the magnetic part of $C_{\text{mag}}$ up to the Néel temperature is reduced about 40% from the theoretical value, showing that Ce$_5$Pb$_3$ is an antiferromagnetic heavy fermion compound.

References