Single Crystal Growth and Low Temperature Magnetic Properties of the Ce-Cu-Al ternary system

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Abstract. We have succeeded in growing BaAl\textsubscript{4}-type CeCu\textsubscript{x}Al\textsubscript{4-x} \((x \sim 0.7)\) and ThMn\textsubscript{12}-type CeCu\textsubscript{4}Al\textsubscript{8} by Al self-flux method for the first time, and the magnetic susceptibility \(\chi\) and electrical resistivity \(\rho\) have been measured. These measurements indicate that CeCu\textsubscript{x}Al\textsubscript{4-x} is a ferromagnet with the Curie temperature of 3.7 K, and another unknown phase transition appears at \(T_0=6.8\) K as an abrupt increase in \(\rho\). This latter transition is probably not due to magnetic origin, because \(\chi\) does not show any anomalies at around \(T_0\). CeCu\textsubscript{4}Al\textsubscript{8} orders antiferromagnetically below 4.7 K. We have performed crystalline electric field analysis from the anisotropy in \(\chi\), and clarified that Kondo effect plays an important role especially for CeCu\textsubscript{4}Al\textsubscript{8}.

1. Introduction

CeCu\textsubscript{6} and CeAl\textsubscript{3} are typical heavy fermion (HF) system. Besides these compounds, Ce-Cu and Ce-Al binary systems include many HF system such as CeAl\textsubscript{2}, Ce\textsubscript{2}Al\textsubscript{11}, CeCu\textsubscript{2}, CeCu\textsubscript{5}. The \(f-d\) hybridization and \(p-f\) mixing play an important role of the formation of HF for Ce-Cu and Ce-Al system, respectively. Thus, we can expect that the Ce-Cu-Al ternary system contains interesting materials. In fact, the system includes an HF antiferromagnet BaNiSn\textsubscript{3}-type CeCuAl\textsubscript{3} with no inversion symmetry [1] and an HF antiferromagnet ThMn\textsubscript{12}-type CeCu\textsubscript{4}Al\textsubscript{8} near a quantum critical point [2], and non magnetic HF Ce\textsubscript{2}Cu\textsubscript{8}Al\textsubscript{9} [3] which is similar to CeCu\textsubscript{6}. Detailed studies of these compounds, however, have not been performed yet due to the difficulty of their single crystal growth.

We have succeeded to grow single crystals of CeCuAl\textsubscript{3} and CeCu\textsubscript{4}Al\textsubscript{8} by Al self-flux method for the first time. In this paper, we describe the crystal growth method and clarify their magnetic and electrical properties, and further determine their crystalline electric field (CEF) level schemes.

2. Experimental

Single crystals were grown by using Al self-flux method. Various starting compositions of constituent elements of Ce, Cu and Al were put into an alumina crucible and stuffed with quartz wool, and then they were sealed in an evacuated quartz ampoule. We adopted the same growing procedure, i.e., the sealed ampoule was heated to 1000 °C and then cooled to 700 °C at a rate of 15 °C/h. Al flux was removed by centrifugation, and the remaining flux was
completely removed by 5 M NaOH solution. Relationship between starting composition and resulting single crystals are shown in Fig. 1. The crystal structure analysis was made by X-ray diffraction, and the resulting single crystals were identified as BaAl$_4$-type CeCu$_{x}$Al$_{4-x}$ ($x \sim 0.7$) and CeCu$_4$Al$_8$, where $x$ was estimated by comparing with lattice constant of polycrystalline CeCu$_x$Al$_{4-x}$. Both crystals were square plate shape with approximate dimension of $2 \times 2 \times 0.5$ mm$^3$. The optimum starting compositions of CeCuAl$_3$ and CeCu$_4$Al$_8$ were CeCu$_{2}$Al$_{15}$ and CeCu$_6$Al$_{30}$, respectively. The magnetization was measured by using a SQUID magnetometer (Quantum Design, MPMS-XL). The electrical resistivity was measured using a standard ac four-probe method in a frequency of 40 Hz and in an effective current of 3 mA.

3. Results and Discussion

Figure 2 shows the temperature dependence of the magnetic susceptibility $\chi$ of CeCu$_{x}$Al$_{4-x}$ ($x \sim 0.7$) and CeCu$_4$Al$_8$. The easy axis is $a$-axis for each compound. For CeCu$_{x}$Al$_{4-x}$, $\chi$ increases rapidly with decreasing temperature below about 5 K (Fig. 2(a)), and the isothermal magnetization curve is non-linear in the same temperature region (not shown). In addition, our preliminary ac susceptibility measurement indicates that the real part shows a divergent behavior at 3.7 K and the imaginary part emerges at around the temperature. These results indicate that CeCu$_{x}$Al$_{4-x}$ is a ferromagnet with the Curie temperature $T_C=3.7$ K. On the other hand, the isothermal magnetization curve of CeCu$_4$Al$_8$ is linear and $\chi$ shows a peak at 4.7 K, indicating that CeCu$_4$Al$_8$ is an antiferromagnet with the Néel temperature $T_N=4.7$ K. However, unlike typical localized antiferromagnet, $\chi_c$ (perpendicular to the easy axis) decreases below $T_N$ and the extrapolation value of $\chi_a$ (parallel to the easy axis) to $T=0$ K remains relatively large.

Figure 3 shows $1/\chi$ vs $T$ plot. Above about 100 K, $\chi(T)$ of each compound follows the Curie-Weiss law with the effective moment of $2.78 \mu_B$/Ce ($a$-axis) and $2.61 \mu_B$/Ce ($c$-axis) for CeCu$_{x}$Al$_{4-x}$, $2.66 \mu_B$/Ce ($a$-axis) and $2.76 \mu_B$/Ce ($c$-axis) for CeCu$_4$Al$_8$, whose values are close to the free ion value for Ce$^{3+}$ of 2.54 $\mu_B$/Ce. Deviation from the Curie-Weiss law below about 100 K is mainly due to CEF effect. Each compound adopts tetragonal crystal structure and the Hamiltonian $\mathcal{H}_{CEF}$ is expressed as

$$\mathcal{H}_{CEF} = B_2^0 O_{2}^0 + B_4^0 O_{4}^0 + B_4^4 O_{4}^4,$$

where $B_n^m$ is CEF parameter and $O_n^m$ Steven’s equivalent operator. The paramagnetic
Figure 2. $\chi$ vs $T$ in a field of 0.1 T along the $a$-axis (open circles) and $c$-axis (closed circles) for (a) CeCu$_{x}$Al$_{4-x}$ ($x \sim 0.7$) and (b) CeCu$_4$Al$_8$. Note that $\chi$ is actually $M/H$ in this figure. The inset shows low temperature portion.

Figure 3. $1/\chi$ vs $T$ in a field of 0.1 T along the $a$-axis (open circles) and $c$-axis (closed circles) for (a) CeCu$_{x}$Al$_{4-x}$ ($x \sim 0.7$) and (b) CeCu$_4$Al$_8$, where the susceptibility of the corresponding La-compounds were subtracted as non magnetic contribution. The solid lines indicate calculated lines based on CEF model. The obtained CEF level scheme and eigenfunction are depicted in the inset, where $\lambda = 0.48$ and $\beta = 0.87$.

susceptibility is described as $\chi = \chi_{CEF}/(1 - \lambda \chi_{CEF})$, where $\chi_{CEF}$ is the CEF susceptibility without magnetic interactions, $\lambda$ the molecular field constant. The calculations were performed by the Levenberg-Marquart least square method. The resulting fitting curves are shown by the solid lines in Fig. 3. The CEF level scheme and the corresponding eigenfunctions are also depicted. The obtained CEF parameters are as follows: $B_{0}^{0}=8.43$ K, $B_{0}^{1}=0.25$ K, $B_{1}^{4}=-0.00$ K, $\lambda_{a}=-0.2$, $\lambda_{c}=0.0$ for CeCu$_{x}$Al$_{4-x}$; $B_{0}^{0}=7.00$ K, $B_{0}^{1}=0.60$ K, $B_{1}^{4}=6.50$ K, $\lambda_{a}=-65$, $\lambda_{c}=-50$ for CeCu$_4$Al$_8$. We point out here CeCuAl$_3$ is an antiferromagnet with $T_N \sim 3$ K and the CEF ground state $| \pm \frac{1}{2} > [1]$. We also note that the replacement of Cu by Al in CeCuAl$_3$ changes magnetic ordering from antiferromagnetic to ferromagnetic [5]. Therefore, CEF ground state of
CeCu$_x$Al$_{4-x}$ changes from $|\pm 1/2>$ to $|\pm 3/2>$ with decreasing $x$, and the change may induce ferromagnetic transition. The experimental results for both compounds are reproduced quite well, but large negative $\lambda$ value for CeCu$_4$Al$_8$ implies the presence of strong Kondo interaction.

Figure 4(a) shows $\rho(T)$ of CeCu$_x$Al$_{4-x}$. As shown in the inset, a slight inflection at $T_C$ and an abrupt increase at $T_0=6.8$ K can be observed. Since the magnetic measurement does not indicate any anomaly at around $T_C$, the transition is not magnetic origin. The open circles indicate magnetic contribution of $\rho$ and the dashed line is the calculated spin disorder resistivity [5], they agree quite well except for low temperature region probably due to Kondo effect. Figure 4(b) shows $\rho(T)$ of CeCu$_4$Al$_8$. The peak temperature in $\rho(T)$ corresponds to $T_N$ determined by magnetization measurements. The magnetic contribution of $\rho$ (open circles) is described quite well by spin disorder resistivity above 50 K. The large deviation indicates the importance of Kondo effect, which agrees well large molecular field constant $\lambda$ derived from CEF analysis of $\chi$. The observed large residual resistivity implies that the constituent composition deviates from CeCu$_4$Al$_8$.

4. Summary
We have succeeded to grow single crystals of CeCu$_x$Al$_{4-x}$ ($x \sim 0.7$) and CeCu$_4$Al$_8$ for the first time. The former compound is a ferromagnet with the Curie temperature $T_C=3.7$ K and another unknown transition at $T_0=6.8$ K. The latter compound is an antiferromagnet with the Néel temperature $T_N=4.7$ K. We have determined their CEF level scheme and clarified an important role of Kondo effect.

References
[1] Kontani M, Ido H, Ando H, Nishioka T and Yamaguchi Y 1994 J. Phys. Soc. Jpn. 63 2503
[2] Gottwick U, Held R, Sparn G, Steglich F, Vey K, Assmus W, Rietschel H, Stewart G R and Giorgi A L 1987 J. Magn. Magn. Mater. 63-64 341
[3] Ido H, Nishioka T and Kontani M 1997 J. Phys. Soc. Jpn. 66 1465
[4] Motoyama G, Murase K and Kontani 1999 JJAP series 11 257
[5] Hessel Andersen N, Gregers-Hansen R E, Holm E, and Smith H and Vogt O 1974 Phys. Rev. Lett. 32 1321