Single crystal growth and magnetic properties of R Cu9Sn4 (R: rare earth metals)

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Abstract. We succeeded in growing single crystals of tetragonal RCu9Sn4 (R=La, Ce, Pr, and Eu) by the Sn-self-flux method for the first time, and studied the electrical and magnetic properties of these compounds. The magnetism of CeCu9Sn4 and PrCu9Sn4 indicates an Ising anisotropy with the magnetic easy axis parallel to the [001] direction. We revealed that EuCu9Sn4 shows an antiferromagnetic transition with an easy plane type magnetic anisotropy in the present single crystal study.

1. Introduction

RCu9Sn4 (R: rare earth metals) crystallizes in the tetragonal LaFe9Si4 type structure with a large distance between R atoms (dR ≃ 6.1 Å) [1, 2], as shown in Fig. 1(a). Polycrystals of R = Ce, Pr, Nd, and Eu are reported as ferromagnets with the Curie temperature TC = 5.5, 10.5, 15 and 10.5 K, respectively, from the electrical resistivity, magnetization, magnetic susceptibility, and specific heat measurements[1, 2]. The magnetic susceptibility follows the Curie-Weiss (C-W) law at high temperatures with the effective magnetic moment μeff = 2.46, 3.41, 3.53, and 7.96 μB, and the paramagnetic Curie temperature θp = -14.5, 13.4, 11.1, and 7 K for CeCu9Sn4, PrCu9Sn4, NdCu9Sn4, and EuCu9Sn4, respectively. The obtained effective magnetic moments correspond to the free ion values of Ce3+, Pr3+, and Nd3+, and the divalent Eu2+ state. In spite of the negative θp, CeCu9Sn4 shows a ferromagnetic ordering. In addition, most of rare earth compounds RCu9Sn4 show the ferromagnetic order. In many cases, a ferromagnetic ground state of Ce compounds can be changed into an antiferromagnetic or non-magnetic ground state by substituting Pr or Nd, as in RRu2Ge2 and RPD2Ga3 for example[3, 4]. In order to investigate the anisotropy and understand the magnetism of RCu9Sn4, we grew the single crystals and measured the electrical resistivity, magnetic susceptibility, and magnetization of these compounds.

2. Experimental

Single crystals of RCu9Sn4 (R=La, Ce, Pr, and Eu) were grown by the Sn-self-flux method under vacuum from the materials of 99.9 % pure (3N)-R, 5N-Cu, and 5N-Sn. These materials were put in an alumina crucible with an off-stoichiometric atomic ratio, R:Cu:Sn = 1:9:10-25.
The crucible sealed in a quartz ampoule was heated to 1050 °C. After 24 hours, the furnace was cooled to 400-600 °C over 3 weeks. The excess Sn-flux was removed by centrifuge. Figure 1(b) shows photographs of single crystals of RCu$_9$Sn$_4$ with a typical size of about 2×2×0.5 mm$^3$, where a flat plane corresponds to the (001) plane. We could not obtain NdCu$_9$Sn$_4$ by the same method, but got binary compounds of Cu-Sn or NdCu$_2$Sn$_2$. The ternary phase diagram of Nd-Cu-Sn indicates the difficulty in growing the crystal of NdCu$_9$Sn$_4$[5].

The electrical resistivity was measured by the ordinary 4-probe AC method. The magnetic susceptibility and magnetization were measured using a commercial SQUID magnetometer. The single-crystal X-ray diffraction measurement was carried out using a diffractometer with graphite monochromated Mo-K$_\alpha$ radiation. The crystal structures of obtained single crystals were confirmed to be the tetragonal LaFe$_9$Si$_4$ type structure, which is ordered derivative of the NaZn$_{13}$ structure as reported in Refs.[1, 2], as shown in Fig. 1(a). The observed lattice parameters of $a \sim 8.6$ Å and $c \sim 12.4$ Å are in good agreement with the previous ones. Details of the crystal structure data will be published elsewhere.

3. Experimental results and discussion

3.1. Electrical resistivity

Figures 2(a) and 2(b) show the temperature dependences of the electrical resistivity $\rho$ of RCu$_9$Sn$_4$ with R = La, Ce, Pr, and Eu for the current $J$ along the [001] direction. The electrical resistivity of all samples decreases monotonically with decreasing temperature. At low temperatures, $\rho$ of R=Ce, Pr, and Eu indicates an abrupt decrease below a magnetic transition temperature indicated by arrows in Fig. 2(b). These magnetic transitions correspond to ferromagnetic orderings for R = Ce ($T_C = 6.6$ K) and Pr ($T_C = 12.0$ K) and an antiferromagnetic one for R = Eu (Néel temperature $T_N = 8.7$ K). The observed ordering temperatures for R = Ce and Pr are higher than the previous values. On the other hand, the present $T_N$ of R = Eu is lower than that of the polycrystalline sample[2]. Note that EuCu$_9$Sn$_4$ is found to be an antiferromagnet as discussed below in contrast to the previous paper reported by Mazzone et al.[2].

The magnetic contribution of the electrical resistivity $\rho_{\text{mag}}$ is obtained by subtracting the lattice contribution $\rho$ (LaCu$_9$Sn$_4$) from $\rho$ (RCu$_9$Sn$_4$), as shown in Fig. 2(c). As the temperature decreases, $\rho_{\text{mag}}$ of Ce and Pr compounds decreases, which is due to a reduction of the magnetic spin scattering derived from the crystalline electric field (CEF) excitation. For EuCu$_9$Sn$_4$, $\rho_{\text{mag}}$ is almost constant above $T_N$, which is mainly due to the disorder of 4f magnetic moments.
Reflecting the orbital angular momentum $L = 0$ in Eu$^{2+}$ state, the CEF splitting does not occur in EuCu$_9$Sn$_4$. Note that a trend is found that absolute value of the electrical resistivity $\rho_{[001]}$ for $J \parallel [001]$ is about twice as large as $\rho_{[100]}$ and $\rho_{[110]}$ (not shown here).

![Graph](image)

**Figure 2.** (a) Temperature dependences of the electrical resistivity and (b) the low-temperature resistivity for the current $J$ along the [001] direction of RCu$_9$Sn$_4$ for R = La, Ce, Pr, and Eu. Arrows indicate the magnetic ordering temperatures. (c) Temperature dependences of $\rho_{\text{mag}} = \rho(\text{RCu}_9\text{Sn}_4) - \rho(\text{LaCu}_9\text{Sn}_4)$ for R = Ce, Pr, and Eu.

### 3.2. Magnetic properties

#### 3.2.1. CeCu$_9$Sn$_4$

Figures 3(a) and 3(b) show the inverse magnetic susceptibility data $1/\chi$ at 0.5 T and the magnetization curves at 2.0 K of CeCu$_9$Sn$_4$, respectively, for the magnetic field $H \parallel [001]$ and [100]. At high temperatures above 150 K, $1/\chi$ follows the C-W law with $\mu_{\text{eff}} = 2.45$ and 2.45 $\mu_B$, and $\theta_P = 26$ and -83 K for $H \parallel [001]$ and [100], respectively. The obtained effective moments are consistent with the result of the polycrystalline experiment[1], where Singh et al. reported that the negative $\theta_P$ is attributed to a peculiarity of the magnetic structure of CeCu$_9$Sn$_4$. However, the negative $\theta_P$ is also affected by the CEF effect. The anisotropy of the magnetic interaction might be small, which will be discussed in EuCu$_9$Sn$_4$. 


The magnetization curve of CeCu$_6$Sn$_4$ indicates a strong Ising anisotropy. The magnetization along the [001] direction $M_{[001]}$ saturates at 0.1 T with a hysteresis and reaches 1.75 $\mu_B$, which is about ten times as large as $M_{[100]}$ at 1 T. The strong Ising anisotropy has also been observed in ferromagnetic compounds such as tetragonal CeRu$_2$Ge$_2$ and CeRu$_2$Al$_2$B$_2$[6–8], where the large anisotropy was well explained by the $\Gamma^1_d$-doublet ground state with the first excited state $\Gamma_6$ at about 500 K. Here, $\Gamma^1_d$ is consist of $\pm \alpha \{ \pm \frac{3}{2} \} \pm \sqrt{1-\alpha^2} \{ \mp \frac{3}{2} \}$ ($\alpha$ is a constant from 0 to 1 determined by the CEF parameters). The value of $\alpha$ in both compounds is very close to 1, which leads to the Ising anisotropy. In CeCu$_6$Sn$_4$, the $\Gamma^1_d$ doublet with $\alpha \sim 1$ is probably the ground state, and the first excited state $\Gamma_6$ is estimated to be at about 100 K, which is much smaller than that of CeRu$_2$Ge$_2$ and CeRu$_2$Al$_2$B. In addition to ferromagnetic transition, these compounds indicate antiferromagnetic one above $T_C$. On the other hand, CeCu$_6$Sn$_4$ indicates a ferromagnetic transition without an antiferromagnetic one. The long $d_R$ ($\sim 6$ Å) in CeCu$_6$Sn$_4$ might suppress the antiferromagnetic interaction. Here, the $d_R$ of CeRu$_2$Ge$_2$ and CeRu$_2$Al$_2$B is about 4 Å.

3.2.2. PrCu$_6$Sn$_4$

The temperature dependences of $1/\chi$ at 0.5 T and the magnetization at 2 K of PrCu$_6$Sn$_4$ are shown in Figs. 3(c) and 3(d), respectively. From the C-W fitting at temperatures higher than 150 K, we obtained $\mu_{\text{eff}} = 3.22$ and 3.45 $\mu_B$, and $\theta_P = 60$ and -47 K for $H \parallel [001]$ and [100], respectively, which are in agreement with the previous study[1]. The magnetization of PrCu$_6$Sn$_4$ also indicates an Ising anisotropy with the easy magnetization axis parallel to the [001] direction. There is a small number of the single crystal studies for Pr based ferromagnetic compounds. The tetragonal PrRu$_2$Si$_2$ is one of examples with $T_C = 14$ K[9]. PrRu$_2$Si$_2$ indicates a uniaxial anisotropy similar to PrCu$_6$Sn$_4$. The anisotropy of PrRu$_2$Si$_2$ is understood by considering the singlet ground state $\Gamma^1_1$ which contains a large magnetic moment state $|\pm 4\rangle$ with the 1st excited singlet $\Gamma_2$ located at an energy comparable to the exchange interaction $k_BT_C[9]$. The $\Gamma_2$ and $\Gamma^1_1$ behave as a quasi-doublet and they split below $T_C$. We could apply the similar CEF scheme with a smaller total energy splitting to PrCu$_6$Sn$_4$, since the magnetic susceptibility of PrCu$_6$Sn$_4$ follows the C-W law with the free ion value of the effective magnetic moment of Pr$^{3+}$ in contrast to that of PrRu$_2$Si$_2$ with the highest splitting energy of 1500 K[10].

3.2.3. EuCu$_6$Sn$_4$

Figures 3(e) and 3(f) show the temperature dependences of $1/\chi$ at 0.5 T and the magnetization curves at 2 K of EuCu$_6$Sn$_4$, respectively. In contrast with CeCu$_6$Sn$_4$ and PrCu$_6$Sn$_4$, EuCu$_6$Sn$_4$ indicates a small anisotropy in the magnetism. In the wide temperature range, $1/\chi$ follows the C-W law with $\mu_{\text{eff}} = 7.92$ and 7.76 $\mu_B$, and $\theta_P = 8.3$ and 9.9 K for $H \parallel [001]$ and [100], respectively, and the obtained effective moments are almost the same with those of the polycrystalline sample[2]. In contrast to the isotropic behavior at high temperatures, we observed a small anisotropy at low temperatures in $\chi$, as shown in the inset of Fig. 3(e). The magnetic susceptibility along the [001] direction $\chi_{[001]}$ continues to increase. On the other hand, $\chi_{[100]}$ indicates a kink at 5 K and decreases with decreasing temperature, meaning that EuCu$_6$Sn$_4$ is the antiferromagnet with an easy plane type magnetic anisotropy. At the low magnetic field of 0.05 T, $\chi_{[001]}$ becomes constant below 8 K, and $\chi_{[100]}$ shows the maximum at about 8 K, which corresponds to $T_N$ observed in the electrical resistivity without magnetic field. The magnetization at 2 K reaches the saturation magnetic moment of 7$\mu_B$ for Eu$^{2+}$ at the critical field $H_C = 0.3$ T (0.75 T) for $H \parallel [001]$ ([100]) without a hysteresis, as shown in Fig. 3(f). The extremely small $H_C$ value compared with $T_N$ is well explained by the two-sublattice model leading to a relation, $H_C = \frac{\alpha \mu_B}{3\mu_B} |T_N - \theta_P| [11]$. EuCu$_6$Sn$_4$ also follows this equation as other antiferromagnetic Eu compounds, as shown in Fig. 3(g). Figure 3(h) shows the geometry of rare
earth metals R in RCu$_9$Sn$_4$. The nearest neighbor R atoms are connected by thick solid lines in the (001) plane, and the second nearest neighbor R atoms are connected by dotted lines along the [001] direction. One of the possible origins of the positive $\theta_P$ in EuCu$_9$Sn$_4$, which leads to the small $H_C$, is due to that the number of ferromagnetic interaction in the (001) plane is twice as many as antiferromagnetic one between (001) planes.

4. Summary
We succeeded in growing the single crystals of RCu$_9$Sn$_4$ (R=La, Ce, Pr, and Eu) and measured the electrical resistivity, magnetic susceptibility, and magnetization of these compounds. In the present single crystal study, we found that CeCu$_9$Sn$_4$ and PrCu$_9$Sn$_4$ indicate the Ising anisotropy along the [001] direction reflecting the CEF effect, and that EuCu$_9$Sn$_4$ is the antiferromagnet with the easy plane type anisotropy perpendicular to the [001] direction. The small critical field $H_C$ of EuCu$_9$Sn$_4$ is found to be well explained by the two sublattice model.

We expect that the CEF split of CeCu$_9$Sn$_4$ and PrCu$_9$Sn$_4$ is smaller than those of other tetragonal ferromagnetic compounds such as CeRu$_2$Ge$_2$ and PrRu$_2$Si$_2$. One of origins of the small CEF split might be due to that Ce or Pr ion in RCu$_9$Sn$_4$ is surrounded by 16 Cu and 8 Sn atoms forming a slightly-distorted snub cube. The exchange interaction $J_{ex}$ in rare earth metal-based intermetallic compounds is based on the RKKY interaction, where $J_{ex}$ depends on $d_R$ and Fermi wave number $k_F$, following the equation: $J_{ex} \propto \sin (2k_Fd_R) - 2k_Fd_R \cos (2k_Fd_R)$. In order to discuss the magnetism of these compounds in details, further precise experiments are necessary.

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References
[1] Singh S, Fornasini M, Manfrinetti P, Palenzona A, Dhar S and Paulose P 2001 J. Alloys Compd. 317-318 560
[2] Mazzone D, Paulose P, Dhar S, Fornasini M and Manfrinetti P 2008 J. Alloys Compd. 453 24
[3] Felner I and Nowik I 1985 J. Phys. Chem. Solids 46 681
[4] Bauer E, Liendl M, Naber L, Werner D, Michor H, Hilsgen G, Donni A, Fischer P, Fauth F and Zollikier M 1997 Z. Phys. B 102 291
[5] Rianip, Fornasini M, Marazza R, Mazzone D, Zanichchi G and Ferro R 1999 Intermetallics 7 835
[6] Raymond S, Haen P, Calemczuk R, Kambe S, Fak B, Lejay P, Fukushima T and Flouquet J 1999 J. Phys.: Cond. Matt. 11 5547
[7] Loidl A, Knorr K, Knopp G, Krimmel A, Caspary R, Böhm A, Sparr G, Geibel C, Steglich F and Murani A 1992 Phys. Rev. B 46 9341
[8] Matsuno H, Nohara H, Kotegawa H, Matsuoka E, Tomiyama Y, Sugawara H, Harima H and Tou H 2012 J. Phys. Soc. Jpn. 81 073705
[9] Mulders A M, Yacouane A, Dalmas de Réotier P, Gubbens P C M, Moolenaar A A, Faks B, Ressouche E, Prešek K, Menovsky A A and Buschow K H J 1997 Phys. Rev. B 56 8752
[10] Michalski R, Kopka Z and Radwański R J 2000 J. Phys.: Cond. Matt. 12 7609
[11] Aoki D, Katayama Y, Settai R, Suzuki N, Sugiyama K, Kindo K, Harima H and Ōnuki Y 1998 J. Phys. Soc. Jpn. 67 4251
[12] Nakamura A, Hiranaka Y, Hedo M, Nakama T, Miura Y, Tsutsui H, Mori A, Ishida K, Mitamura K, Hirose Y, Sugiyama K, Honda F, Settai R, Takeuchi T, Hagiwara M, D Matsuda T, Yamamoto E, Haga Y, Matsubayashi K, Uwatoko Y, Harima H and Ōnuki Y 2013 J. Phys. Soc. Jpn. 82 104703
[13] Nakamura A, Hiranaka Y, Hedo M, Nakama T, Tatetsuy Y, Maehira T, Miura Y, Mori A, Tsutsui H, Hirose Y, Mitamura K, Sugiyama K, Hagiwara M, Honda F, Takeuchi T, Haga Y, Matsubayashi K, Uwatoko Y and Ōnuki Y 2013 J. Phys. Soc. Jpn. 82 124708
Figure 3. Temperature dependences of the inverse magnetic susceptibility at 0.5 T ((a), (c), (e)) and the magnetization curves at 2.0 K ((b), (d), (f)) for $H \parallel [001]$ (red circles) and $[100]$ (black circles) of $\text{CeCu}_9\text{Sn}_4$, $\text{PrCu}_9\text{Sn}_4$, and $\text{EuCu}_9\text{Sn}_4$. The solid lines in (a), (c), and (e) are obtained by the C-W fitting. The inset of (e) shows the magnetic susceptibility of $\text{EuCu}_9\text{Sn}_4$ at 0.5 T. (g) $H_C$ vs $|T_N - \theta_P|$ for several Eu compounds (black circles) cited from Refs. [11–13] with the theoretical solid line. (h) The geometry of rare earth metals (R) in $\text{RCu}_9\text{Sn}_4$. Thin solid lines show the unit cell. The nearest neighbor R atoms in (001) plane and the second nearest neighbor R atoms along the [001] direction are connected by thick solid and dotted lines, respectively.