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# Single-crystal growth of layered Ce–Ni–Ge ternary compounds

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**Abstract**

We have attempted to grow single crystals of Ce–Ni–Ge ternary system having layered structure. Several polycrystalline samples, $CeNiGe_x$ ($2 < x < 3$), $Ce_3Ni_xGe_y$ ($1.6 < x < 2$, $6.5 < y < 8.5$) and $Ce_2NiGe_6$, were prepared by an arc-melting of constituent elements. All samples grown by the Czochralsky method are found to contain the phase of the orthorhombic $CeNiGe_2$ type structure. A Rietveld method was applied to analyze the crystal structure of $CeNiGe_{2.2}$ using X-ray powder diffraction data at room temperature. The refined lattice parameters were $a = 4.260$ Å, $b = 16.81$ Å and $c = 4.209$ Å with the space group Cmmm. The temperature dependence of magnetic susceptibility shows a significant variation in the magnetic properties depending on the concentration of Ge, that is, magnetic phase transition temperature depends on starting materials. It may come from the fact that the magnetic property relies on a structural homogeneity and a stoichiometry.


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*Keywords:* Ternary rare earth compounds; $CeNiGe_2$; $CeNiGe_3$; $Ce_3Ni_2Ge_7$; $Ce_2NiGe_6$

## 1. Introduction

A lot of investigations have been reported on a series of ternary compounds $Ce_xT_yX_z$ (T: a transition metal and X: a *p* element). In these compounds, the Ruderman–Kittel–Kasuya–Yoshida (RKKY) interaction and Kondo effect compete each other. Competition between the RKKY interaction and Kondo effect was discussed by Doniach as a function of $|J_{cf}|D(\epsilon_F)$, where $|J_{cf}|$ is the magnitude of the magnetic c–f exchange interaction and $D(\epsilon_F)$ is the density of the states at the Fermi energy $\epsilon_F$ [1]. The external pressure is one of the control parameters to tune the value $|J_{cf}|$, which leads a long range magnetically ordered state, or results in a screening of the 4f moment by conduction electrons. For example, when pressure is applied to the compounds having antiferromagnetic ordering such as $CePd_2Si_2$, $CeRh_2Si_2$ and $CeRhIn_5$, the Néel temperature $T_N$ decreases to zero and a quantum critical point is reached [2], in which quasi-two dimensional electronic state and magnetic instability play an important role.

Recently Salamakha et al., have identified 20 ternary germanides in the Ce–Ni–Ge system [3]. Durivault et al. summarized the physical properties of these ternary germanides in order to determine the influence of chemical composition [4]. It has been revealed that several compounds have antiferromagnetic ordering and layered structure such as $Ce_2NiGe_6$ (a Néel temperature $T_N = 10.4$ K [6]), $Ce_3Ni_2Ge_7$ ($T_N = 7.2$ K [7]), $CeNiGe_2$ ($T_{N1} = 3.9$ K and $T_{N2} = 3.2$ K [8]) and $CeNiGe_3$ ($T_N = 5.5$ K [9]), which have a quasi-two dimensional electronic state and are expected to have competition between the RKKY interaction and Kondo effect. In

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Fig. 1. Photograph of a single crystal ingot of $CeNiGe_2$.

this paper, we attempt to prepare the single crystal of Ce–Ni–Ge system having layered structure in order to get deep insight about the electronic and magnetic properties of these compounds.

## 2. Experimental

The polycrystalline samples, $Ce_2NiGe_6$, $Ce_3Ni_xGe_y$ ($1.6 < x < 2.0$, $6.5 < y < 8.5$), $CeNiGe_x$ ($2 < x < 3$) were prepared as starting materials by arc-melting cerium (99.9%), nickel (99.99%) and germanium (99.999%) in a tetra-arc furnace under argon atmosphere. To improve homogenity, the ingot was turned over and remelted several times. The weight loss is negligible. Single crystals were grown by a Czochralski pulling method. The pulling parameter was kept constant during the growth (pulling rate: 10 mm/h; seed rotation speed: 10 rpm; crucible-rotation speed: 5 rpm). An ingot was 3–4 mm in diameter and 50 mm in length as shown in Fig. 1. The samples were annealed for 2 weeks in a quartz tube under the vacuum of $1 \times 10^{-6}$ Torr at 800 °C.

The samples were checked by conventional X-ray powder diffraction experiments using Cu Kα radiation. The crystal structure was refined by the Rietveld profile method by using the RIETAN-2000 program [5]. The single crystalline state was confirmed using back-scattering Laue technique. Its homogeneity and chemical composition were checked by microprobe analysis, which was made using SEM(SS-550) at the Center of Advanced Instrumental Analysis, Kyushu University, based on the measurement of the Ce Lα1, Ni Kα1 and Ge Kα1 X-ray emission lines. The dc magnetic susceptibility was measured in the temperature range 2.0–300 K using a Quantum Design MPMS-5 superconducting quantum interference device magnetometer.

## 3. Results and discussion

### 3.1. Crystal structure

By using a microprobe analysis for $Ce_3Ni_2Ge_7$ polycrystalline sample, the experimental atomic percentages are obtained to be Ce 24.1(6)%, Ni 17.9(9)% and Ge 57.8(6)%, respectively. These results are closed to the recent results (Ce 23.6(4)%, Ni 19.7(3)% and Ge 56.7(4)%) [7] and the theoretical value (Ce 25.0%, Ni 16.7% and Ge 58.3%). Those for the single crystalline sample obtained by polycrystalline $Ce_3Ni_2Ge_7$, however, are obtained to be Ce 28.2(9)%, Ni 22.4(6)% and Ge 49.2(5)%, which is closed to the theoretical value of $CeNiGe_2$ (Ce 25.0%, Ni 25.0% and Ge 50.0%) rather than that of $Ce_3Ni_2Ge_7$.

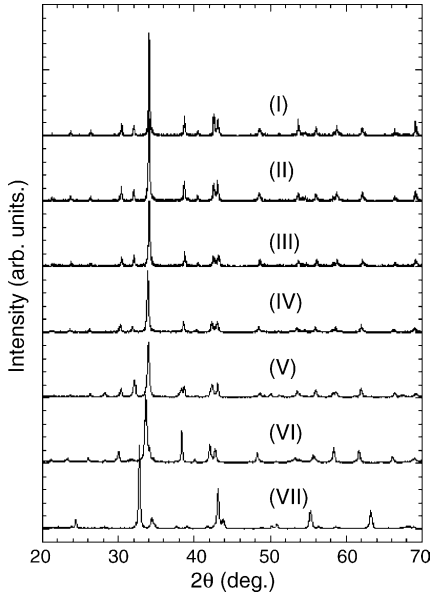


Fig. 2. X-ray powder diffraction pattern of single crystals obtained by polycrystalline (I) $CeNiGe_{2.1}$, (II) $CeNiGe_{2.2}$, (III) $Ce_3Ni_2Ge_{6.5}$, (IV) $Ce_3Ni_2Ge_{7.5}$, (V) $Ce_3Ni_{1.6}Ge_7$, (VI) $Ce_2NiGe_6$ and (VII) $CeNiGe_2$ as starting materials.

Fig. 2 shows X-ray powder diffraction pattern of single crystals obtained by several starting materials. It is found that all samples have same crystal structure except the sample (VII), and contain a large amount of the orthorhombic $CeNiGe_2$ type layered structure (space group Cmcm). It indicates that Ce–Ni–Ge compounds having layered structure do not melt congruently, $CeNiGe_2$ phase melts at highest temperature in these compounds, and that it is easy to grow $CeNiGe_2$ single crystal by a Czochralski pulling method. On the other hand, the single crystal (VII) is not single phase, including hexagonal $Ce_2NiGe_3$ (space group P6/mmm) [11]. It is considered that single crystal of $CeNiGe_2$ grows into the self-flux of Ni or Ge.

The X-ray powder diffraction data of the single crystal by using $CeNiGe_{2.2}$ button was analyzed by the Rietveld profile method. The results are summarized as follows: (i) it exhibits a good chemical homogeneity and is single phase; (ii) $CeNiGe_{2.2}$ crystallizes the orthorhombic $CeNiSi_2$ type layered structure. The atoms are all placed in the 4c position of the space group Cmcm ($D_{2h}^{17}$) with fractional coordinates: Ce (0, 0.108, 0.25), Ni (0, 0.314, 0.25), Ge(1) (0, 0.457, 0.25) and Ge(2) (0, 0.750, 0.25). The lattice parameters along *b*-axis is extremely large compared to those along *a*- and *c*- axes: $a = 4.260$ Å, $b = 16.81$ Å and $c = 4.209$ Å.

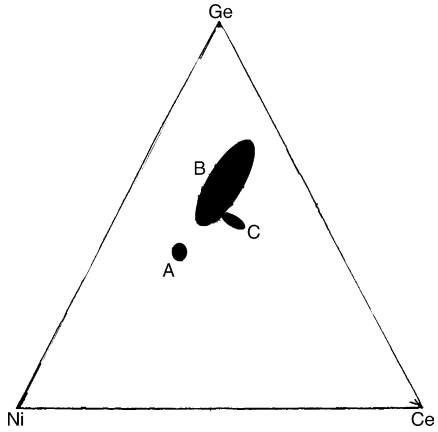


Fig. 3. Schematic diagram showing the composition of ternary compounds in the Ce–Ni–Ge system where single crystal is grown by a Czochralski pulling method; (A) $CeNi_2Ge_2$ [10], (B) $CeNiGe_2$ (this work) and (C) $Ce_2NiGe_3$ [11].

The reliability factors are RWP = 10.29%, RP = 7.23%, Re = 7.96%, RR = 9.54% and $s = 1.293$.

Fig. 3 schematically shows the composition where single crystal is grown by a Czochralski pulling method. Although five ternary compounds have been reported in the region of B ($Ce_2NiGe_6$, $Ce_3Ni_2Ge_7$, $CeNiGe_3$, $CeNiGe_2$ and $Ce_2Ni_3Ge_5$) [3], only the single crystal of $CeNiGe_2$ was grown in this work. A flux-method may be available to obtain other single crystal. Indeed, a single crystal of $CeNiGe_2$ is also grown by using Sn-flux method [8].

### 3.2. Magnetic properties

Fig. 4 shows the temperature dependence of dc-magnetic susceptibility for two samples taken from the ingot (I) and (II), in Fig. 2. The data of both samples exhibits a maximum and a small hump. The magnetic transition temperatures are defined to be $T_1 = 5.2$ K and $T_2 = 3.0$ K for I, and $T_1 = 5.2$ K and $T_2 = 2.4$ K for II. These results are different from the previous one, in which two kinks are clearly visible on the $\chi$–$T$ curve and $T_{N1}$ and $T_{N2}$ are defined to be 3.9 and 3.2 K, respectively [8]. In this connection we would like to mention the results of $CeNiSn_2$ [12]. The refinement of the nuclear structure shows that this compound is slightly Ni-deficient, the corresponding formula being $CeNi_{0.84}Sn_2$. The observation of two magnetic phases is attributed to the occurrence of concentration fluctuations associated with the Ni deficiency. It is indicated that $CeNiGe_2$ also forms a range of solid solutions characterized by some extent of Ni or Ge deficiency, and the magnetic property relies on a structural homogeneity or a stoichiometry.

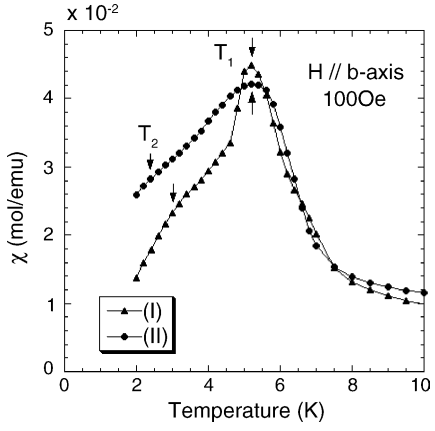


Fig. 4. Magnetic susceptibility of single crystals grown by the ingots of (I) and (II).

## 4. Summary

We have attempted to grow single crystals of Ce–Ni–Ge system having layered structure. Several polycrystal samples $CeNiGe_x$ ($2 < x < 3$), $Ce_3Ni_xGe_y$ ($1.6 < x < 2$, $6.5 < y < 8.5$) and $Ce_2NiGe_6$ were prepared by arc melting from starting elements. All samples contain the phase of the orthorhombic $CeNiGe_2$ type structure. Our results demonstrate a significant variation in the temperature-dependent magnetic susceptibility of single crystals grown by starting materials; $CeNiGe_{2.1}$ and $CeNiGe_{2.2}$. It may come from the fact that the magnetic property relies on a structural homogeneity or a stoichiometry.

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