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# Synthesis and magnetic and electronic properties of metastable non-stoichiometric ThCr$_2$Si$_2$-type ternary Ce–Ni–Ge compound

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**Abstract**
The metastable non-stoichiometric ThCr$_2$Si$_2$-type ternary Ce–Ni–Ge compound has been synthesized via a polymorphic crystallization from Ce$_6$Ni$_{34}$Ge$_{60}$ amorphous alloy. The cell parameters are $a = 4.0659(2)$ Å and $c = 10.6648(6)$ Å. The $c/a$ ratio and cell volume are 2.6230 and 176.3(1) Å$^3$, respectively. The $a$-axis parameter is smaller than that of the stoichiometric CeNi$_2$Ge$_2$, while the $c$-axis parameter and $c/a$ ratio are significantly larger than that of the stoichiometric compound. The temperature dependence of the magnetic susceptibility shows Curie–Weiss-like temperature dependence above 2 K, indicating that there is no magnetic transition above 2 K. The effective magnetic moment, $p_{eff}$, and paramagnetic Curie temperature, $\theta_p$, are $p_{eff} = 2.18 \, \mu_B$ and $\theta_p = -12$ K, respectively. This indicates that the Ce ions are mostly Ce$^{3+}$ and partially Ce$^{4+}$. The electrical resistivity decreases with decreasing temperature and decreases much more below about 110 K. Then, it increases below about 25 K linearly against $\ln(T)$. This is one of the characteristics of a Kondo compound. The thermoelectric power between 80 and 400 K is negative and of several $\mu$V K$^{-1}$, and it shows a broad peak around 110 K.

## 1. Introduction

The ternary RENi$_2$Ge$_2$ compounds (RE = rare earth metals) crystallize in the ThCr$_2$Si$_2$-type structure, as shown in figure 1, which is one of the most common crystal structures found in ternary compounds. It is of a body-centred tetragonal unit cell ($I4/mmm$, space group no. 139). The RE atoms occupy the corner and centre positions. The Ni atoms occupy the Wyckoff site 4d (1/2, 0, 1/4) and form two-dimensional square planes. The Ge atoms occupy the Wyckoff site 4e (0, 0, $z$). Thus, they form GeNi$_4$-square pyramids above and below the two-dimensional square plane alternately. They are connected by the Ge–Ge bond in the two-dimensional square plane. The RE atoms are located in the centre of this framework in which there is a large void. These compounds show interesting physical properties [1–5]. For example, CeNi$_2$Ge$_2$ is a heavy fermion compound with the low-temperature specific heat
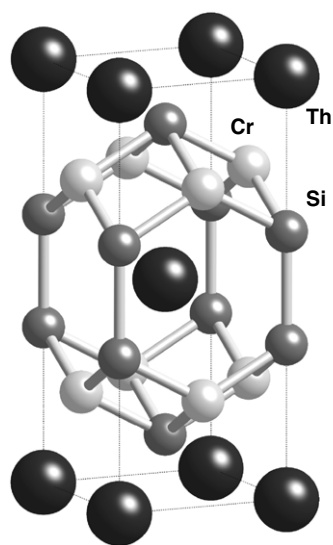
**Figure 1.** Crystal structure of the ternary $ThCr_2Si_2$-type compounds.

coefficient $\gamma = 350$ mJ mol$^{-1}$ K$^{-2}$, and Kondo temperature about 30 K [1]. $NdNi_2Ge_2$ and $TmNi_2Ge_2$ show a complex anti-ferromagnetic state at low temperatures [2, 3]. $TbNi_2Ge_2$ shows two anti-ferromagnetic orderings at 9 and 16 K [4]. $YbNi_2Ge_2$ is a mixed valence compound [5].

Hasegawa *et al* recently obtained a new metastable La–Ge–Ni ternary $ThCr_2Si_2$-type compound by polymorphic crystallization from the $La_6Ni_{34}Ge_{60}$ amorphous alloy [6]. The exact formula of the new compound was $(La_{0.3}Ge_{0.7})$ $(Ni_{0.85}Ge_{0.15})_2Ge_2$, indicating that it was highly non-stoichiometric compared to the stoichiometric $LaNi_2Ge_2$. Since there are several $ThCr_2Si_2$-type $RENi_2Ge_2$ compounds, as mentioned above, it is interesting to investigate the formation of these metastable non-stoichiometric $ThCr_2Si_2$-type ternary RE–Ni–Ge compounds crystallized from $RE_6Ni_{34}Ge_{60}$ amorphous alloys. In this study, Ce is selected as a rare earth metal of $RE_6M_{34}Ge_{60}$ because it has almost the same trivalent ionic radius as La (La$^{3+}$: 1.160 Å (CN = 8), Ce$^{3+}$: 1.143 Å (CN = 8) [7]). In addition, the stoichiometric $ThCr_2Si_2$-type $CeNi_2Ge_2$ shows interesting physical properties, i.e. heavy fermion behaviour [1]. Accordingly, it is also interesting to investigate the physical properties of the highly non-stoichiometric $ThCr_2Si_2$-type ternary Ce–Ni–Ge compound if it is synthesized.

In this study, the metastable non-stoichiometric $ThCr_2Si_2$-type ternary Ce–Ni–Ge compound was successfully synthesized via polymorphic crystallization from $Ce_6Ni_{34}Ge_{60}$ amorphous alloy. The synthesized compound was investigated by x-ray diffraction measurement and differential scanning calorimetry (DSC). Then, its magnetic and electronic properties were also clarified by measuring the temperature dependence of the magnetic susceptibility, electrical resistivity and thermoelectric power. These results are discussed in comparison with the reported results of the metastable non-stoichiometric $ThCr_2Si_2$-type ternary La–Ni–Ge compound and the stoichiometric $CeNi_2Ge_2$.

## 2. Experimental procedure

Mother ingots of $Ce_6Ni_{34}Ge_{60}$ alloys were prepared by the arc melting of a mixture of pure metals Ce (99.9%), Ni (99.99%) and Ge (99.999%) in an argon atmosphere purified using a Ti getter. Alloy ribbons were prepared by the single-roller melt spinning technique in an
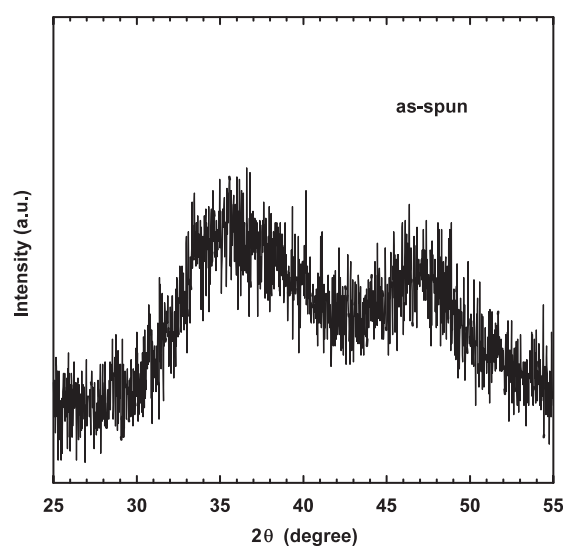
**Figure 2.** X-ray scattering intensity profile of as-spun Ce$_6$Ni$_{34}$Ge$_{60}$ ribbons.

argon atmosphere. The thermal stability and phase transformation were investigated using a differential scanning calorimeter (DSC) at a heating rate of 0.67 K s$^{-1}$ in a purified argon atmosphere. The isothermal annealing of samples was also carried out in the DSC apparatus in a purified argon atmosphere on the basis of the DSC results for 10 min. Phases of the sample were identified by ordinary x-ray powder diffractometry using Cu K$\alpha$ radiation with a Ni filter. The temperature dependence of the DC magnetic susceptibility was measured by using a SQUID magnetometer between 2 and 300 K in a magnetic field of 1 kOe. The temperature dependence of the DC electrical resistivity was measured by the conventional four-probe method between 4.2 and 300 K. The temperature dependence of the thermoelectric power was measured by the conventional DC method between 80 and 400 K. The temperature difference to measure thermoelectric power was about 5 K. The thermoelectric power was measured three times at each temperature and then the averaged value was used for the plotted data.

## 3. Results and discussion

Figure 2 shows an x-ray scattering intensity profile of as-spun ribbons. No diffraction peaks are observed in the profile, indicating an amorphous structure. Figure 3 shows a DSC curve of the as-spun ribbons. The result of the La$_6$Ni$_{34}$Ge$_{60}$ amorphous alloy is also shown for comparison [6]. There is a first sharp exothermic peak at 570 K corresponding to the crystallization and second one at 732 K. It is found that this DSC curve is similar to that of the La$_6$Ni$_{34}$Ge$_{60}$ amorphous alloy although the peak temperatures are different. This suggests that the Ce$_6$Ni$_{34}$Ge$_{60}$ amorphous alloy has a crystallization process the same as that reported for La$_6$Ni$_{34}$Ge$_{60}$ [6].

Figure 4 shows the x-ray powder diffraction patterns of the annealed samples. The result of the reported metastable non-stoichiometric ThCr$_2$Si$_2$-type La–Ni–Ge compound is also shown in the figure 6. Figure 4(b) is of the sample annealed at about 580 K, which just is above the crystallization peak in the DSC curve (figure 3(a)). It is found that the pattern is almost the same as the pattern reported for the non-stoichiometric La–Ni–Ge compound (figure 4(c)). Figure 4(a) is of the sample annealed at about 800 K, which is above the second peak in the DSC
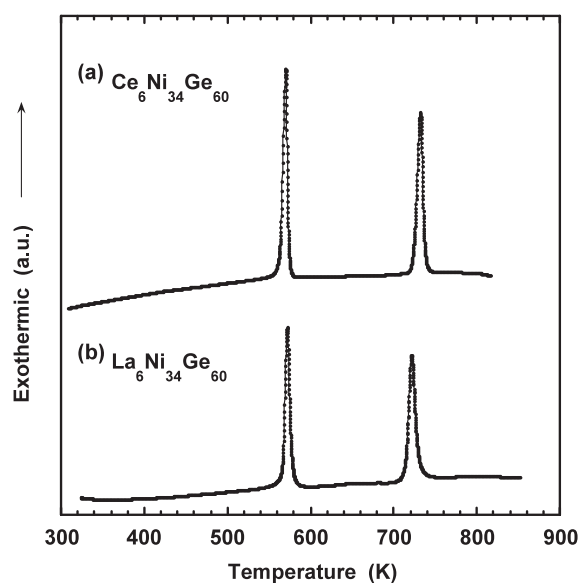
**Figure 3.** DSC curve of $Ce_6Ni_{34}Ge_{60}$ amorphous alloys. The reported result of $La_6Ni_{34}Ge_{60}$ is also shown in the figure for comparison [6]. (a) $Ce_6Ni_{34}Ge_{60}$, (b) $La_6Ni_{34}Ge_{60}$.

curve in figure 3(a). This pattern can be identified by the three stable compounds $CeNi_2Ge_2$ ($ThCr_2Si_2$-type), Ge and GeNi, as marked in figure 4(a), and it is completely different from the pattern in figure 4(b). The composition of the amorphous $Ce_6Ni_{34}Ge_{60}$ alloy in this study is the same as that of the reported $La_6Ni_{34}Ge_{60}$, and the ionic radii of the trivalent Ce (1.18 Å) and La (1.22 Å) ions are almost the same. Accordingly, it can be concluded that the phase crystallized from the amorphous alloy in this study is also a metastable non-stoichiometric $ThCr_2Si_2$-type ternary compound as well as $La_6Ni_{34}Ge_{60}$.

The observed reflection angles were obtained by fitting each diffraction peak using the Gaussian formula. Cell parameters of the phases were calculated by using the least-squares method. The cell parameters of the non-stoichiometric $ThCr_2Si_2$-type ternary Ce–Ni–Ge compound are $a = 4.0659(2)$ Å and $c = 10.6648(6)$ Å. The $c/a$ ratio is 2.6230. The cell volume is calculated to be 176.3(1) Å$^3$. The reported non-stoichiometric $ThCr_2Si_2$-type ternary La–Ni–Ge compound had $a = 4.0745(2)$ Å, $c = 10.6717(7)$ Å and $c/a = 2.6191$, respectively [6]. Compared to these data, both lattice parameters of the former are smaller than those of the latter. This is attributable to the smaller trivalent ionic radius of Ce ion than La ion. However, it is interesting that the $c/a$ ratios are almost the same as each other.

The cell parameters of the stoichiometric $CeNi_2Ge_2$ are $a = 4.150$ Å and $c = 9.842$ Å and its $c/a$ is 2.372 [8]. The $a$-axis parameter of the non-stoichiometric compound in this study is smaller than that of the stoichiometric one, while the $c$-axis parameter is significantly larger than that of the stoichiometric one. In addition, its $c/a$ ratio is significantly larger than that of the stoichiometric $CeNi_2Ge_2$. These relationships of the cell parameters between the non-stoichiometric and stoichiometric $ThCr_2Si_2$-type Ce–Ni–Ge compounds are also obtained in the results of the reported $ThCr_2Si_2$-type La–Ni–Ge compounds [6].
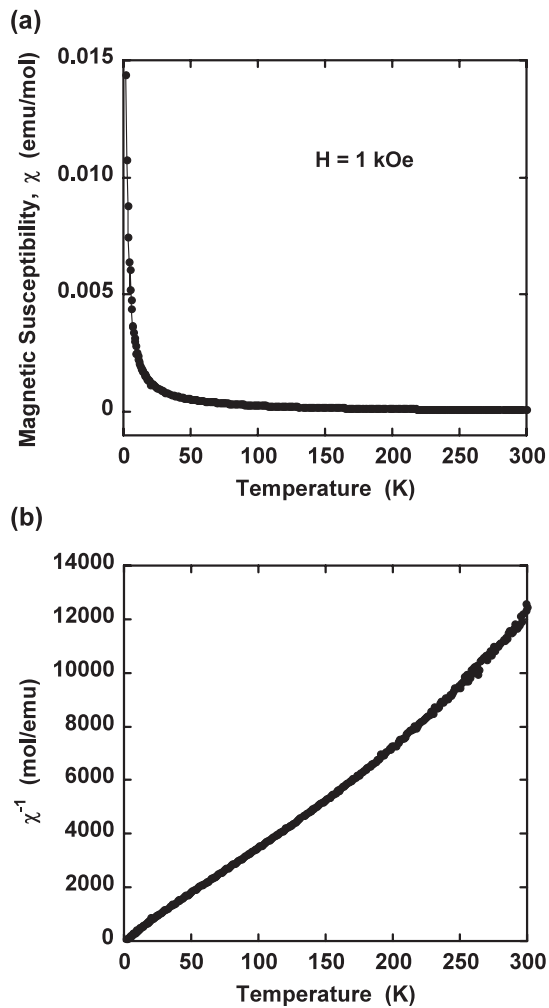
Figure 5 shows the temperature dependence of the magnetic susceptibility of the non-stoichiometric Ce–Ni–Ge compound. The susceptibility is of almost the same magnitude as that of $CeNi_2Ge_2$ and it exhibits Curie–Weiss-like temperature dependence in the whole measured temperature region. This indicates that there is no magnetic transition in the non-stoichiometric Ce–Ni–Ge compound in contrast to the result for the stoichiometric Ce–Ni–Ge compound which shows a weak hump around 30 K due to the peak in the magnetic susceptibility
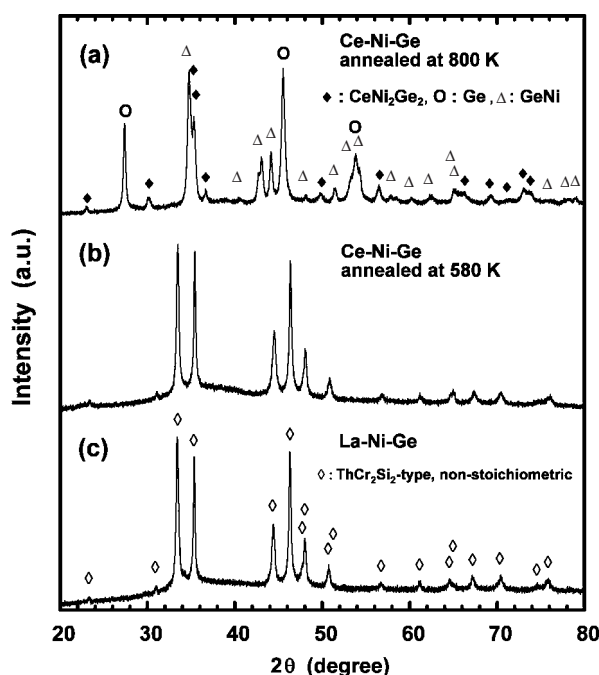
**Figure 4.** X-ray diffraction patterns of samples quenched after being heated above the first and second crystallization peaks in the DSC curve of Ce$_6$Ni$_{34}$Ge$_{60}$. The result of the reported metastable non-stoichiometric ThCr$_2$Si$_2$-type ternary La–Ni–Ge compound is also shown in the figure for comparison [6]. (a) Above the second peak, (b) above the first peak, (c) non-stoichiometric ThCr$_2$Si$_2$-type ternary La–Ni–Ge compound.

parallel to the $c$-axis [9]. Figure 5(b) shows the temperature dependence of the reciprocal magnetic susceptibility. It does not show a complete linear relationship. Accordingly, the temperature dependence is fitted by the equation of the sum of the constant magnetic susceptibility term ($\chi_0$) and the Curie–Weiss law one ($C/(T - \theta_p)$) to estimate the effective magnetic moment, $p_{\text{eff}}$, and paramagnetic Curie temperature, $\theta_p$ using data above 80 K. The calculated values are $p_{\text{eff}} = 2.18 \ \mu_B$ and $\theta_p = -12$ K, respectively. The $p_{\text{eff}}$ value is smaller than the expected values (2.54 $\mu_B$) of the magnetic moment of Ce$^{3+}$. This indicates that the Ce ions of the non-stoichiometric ThCr$_2$Si$_2$-type Ce–Ni–Ge compound in this study have mixed valence, i.e. mostly Ce$^{3+}$ and partially Ce$^{4+}$. The negative value of $\theta_p$ indicates that the magnetic interaction between Ce ions in this compound is anti-ferromagnetic. However, it should be noted that it is a much smaller negative value than the $\theta_p$ of the stoichiometric CeNi$_2$Ge$_2$ ($-112$ K) [9].
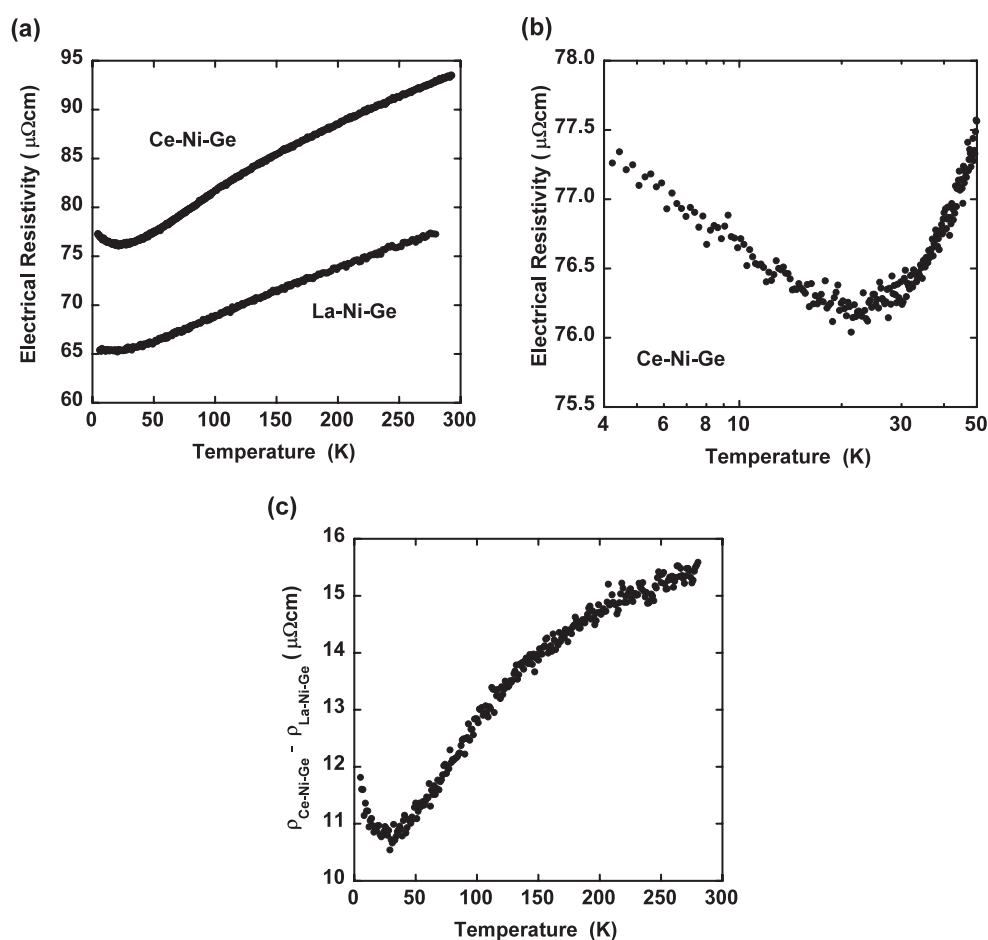
Figure 6(a) shows the temperature dependence of the electrical resistivity. The result of the non-stoichiometric ThCr$_2$Si$_2$-type La–Ni–Ge compound is also shown for comparison [6]. The resistivity decreases with decreasing temperature and decreases much more below about 110 K. Then, it increases below about 25 K, i.e., there is a minimum in the temperature dependence of the electrical resistivity. Figure 6(b) shows the result in the logarithm scale of temperature below 50 K. It is found that the electrical resistivity below the minimum temperature changes linearly against ln($T$). This is one of the characteristics of a Kondo compound, indicating that this non-stoichiometric Ce–Ni–Ge compound is a Kondo compound. Such a minimum behaviour of electrical resistivity was not observed in the result of the

**(a)**



**(b)**



**Figure 5.** Temperature dependence of the magnetic susceptibility (a) and reciprocal magnetic susceptibility (b) of the non-stoichiometric $ThCr_2Si_2$-type ternary Ce–Ni–Ge compound.

stoichiometric $CeNi_2Ge_2$ [10]. Figure 6(c) shows the temperature dependence of the difference of the electrical resistivities between the non-stoichiometric $ThCr_2Si_2$-type Ce–Ni–Ge and La–Ni–Ge compounds which corresponds to the magnetic resistivity. It shows almost the same temperature dependence as the original temperature dependence of the electrical resistivity of the non-stoichiometric Ce–Ni–Ge compound. This is different from the result of the stoichiometric $CeNi_2Ge_2$ which shows a broad peak of the temperature dependence of the electrical resistivity around 100 K [10].

Figure 7 shows the temperature dependence of the thermoelectric power above about 80 K. The thermoelectric power values are negative and small in the whole measured temperature range. This is very different from the result of the stoichiometric $CeNi_2Ge_2$ which shows several dozens of positive thermoelectric power [10]. It increases with decreasing temperature above about 110 K, and then decreases below about 110 K. Therefore, there is a broad peak around 110 K. It is interesting that this broad peak temperature is almost the same as the temperature below which the electrical resistivity decreases significantly downwards, as mentioned above. It is also interesting that the stoichiometric $CeNi_2Ge_2$ also shows a broad peak around 100 K [10] although the magnitude of the thermoelectric power is highly different.
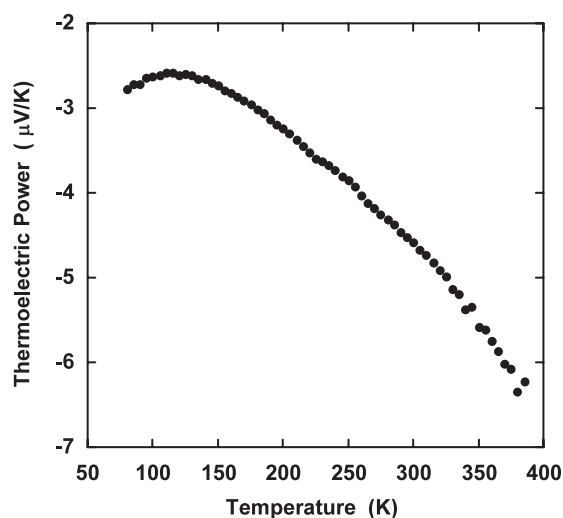
**Figure 6.** (a) Temperature dependence of electrical resistivity of the non-stoichiometric ThCr$_2$Si$_2$-type ternary Ce–Ni–Ge compound. The result of the non-stoichiometric ThCr$_2$Si$_2$-type La–Ni–Ge compound is also shown for comparison [6]. (b) Temperature dependence of electrical resistivity of the non-stoichiometric ThCr$_2$Si$_2$-type ternary Ce–Ni–Ge compound in the logarithmic scale for temperatures below 50 K. (c) Temperature dependence of the difference of the electrical resistivities between the non-stoichiometric ThCr$_2$Si$_2$-type Ce–Ni–Ge ($\rho_{\text{Ce–Ni–Ge}}$) and La–Ni–Ge compounds ($\rho_{\text{La–Ni–Ge}}$) in (a) which corresponds to the magnetic resistivity.

## 4. Conclusion

The metastable non-stoichiometric ThCr$_2$Si$_2$-type ternary Ce–Ni–Ge compound has successfully been synthesized via polymorphic crystallization from Ce$_6$Ni$_{34}$Ge$_{60}$ amorphous alloys. The cell parameters are $a = 4.0659(2)$ Å and $c = 10.6648(6)$ Å. The $c/a$ ratio and cell volume are 2.6230 and 176.3(1) Å$^3$, respectively. The $a$-axis parameter of the non-stoichiometric compound in this study is smaller than that of the stoichiometric CeNi$_2$Ge$_2$, while the $c$-axis parameter is significantly larger than that of the stoichiometric compound. The $c/a$ ratio is also significantly larger. These relationships of the cell parameters between the ThCr$_2$Si$_2$-type non-stoichiometric and stoichiometric Ce–Ni–Ge compounds are also obtained for the reported La–Ni–Ge compounds.

The temperature dependence of the magnetic susceptibility shows Curie–Weiss-like temperature dependence in the whole measured temperature range, indicating that there is no

**Figure 7.** Temperature dependence of the thermoelectric power of the non-stoichiometric ThCr$_2$Si$_2$-type ternary Ce–Ni–Ge compound.

magnetic transition above 2 K. This is different from the result of the stoichiometric compound which shows a weak hump around 30 K due to the peak in the magnetic susceptibility parallel to the *c*-axis. The effective magnetic moment, $p_{eff}$, and paramagnetic Curie temperature, $\theta_p$, are $p_{eff} = 2.18\ \mu_B$ and $\theta_p = -12$ K, respectively. This indicates that the Ce ions are mostly Ce$^{3+}$ and partially Ce$^{4+}$. The electrical resistivity decreases with decreasing temperature and decreases much more below about 110 K. Then, it increases below about 25 K linearly against $\ln(T)$, indicating that the non-stoichiometric ThCr$_2$Si$_2$-type ternary Ce–Ni–Ge compound in this study is a Kondo compound. The thermoelectric power between 80 and 400 K is negative and of several $\mu$V K$^{-1}$. The temperature dependence of the thermoelectric power shows a broad peak around 110 K.

## Acknowledgments

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