

# Enhanced Thermoelectric Power Factors in the $\text{Ce}(\text{Ni}_{1-x}\text{Cu}_x)_2\text{Si}_2$ and $\text{CeNi}_2(\text{Si}_{1-y}\text{Ge}_y)_2$ Alloys

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In the presence of hybridization of the  $f$  states with the conduction electrons Ce-based compounds can show large peaks in the temperature dependence of the Seebeck coefficient, which makes them interesting materials for applications. The Seebeck coefficient and electrical resistivity of the bulk, arc-melted, single phase samples of  $\text{Ce}(\text{Ni}_{1-x}\text{Cu}_x)_2\text{Si}_2$  and  $\text{CeNi}_2(\text{Si}_{1-y}\text{Ge}_y)_2$  alloys were measured over the temperature range of 2 K to 300 K. All the samples exhibited a positive Seebeck coefficient, which reaches up to  $\sim 50\mu\text{V}/\text{K}$  at 150 K and it can be shifted up to 300 K by appropriate doping. The thermoelectric power factor,  $PF = S^2/\rho$ , reached a maximum of  $1.4 \times 10^{-3} \text{ Wm}^{-1}\text{K}^{-2}$  at 290 K and  $1.1 \times 10^{-3} \text{ Wm}^{-1}\text{K}^{-2}$  at 110 K for  $x = 0.25$  and  $y = 0.75$ , respectively. For selected representatives of the studied series thermoelectric properties have been measured up to 1000 K.

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## 1. Introduction

Ce-based materials can show attractive thermoelectric (TE) properties in low temperature regime [1–8] due to the proximity of the  $f$ -electron level to the Fermi energy, resulting in a sharp feature in the electron density of states that gives rise to a large Seebeck coefficient. At low temperature TE devices may find use in the space industry.

In our previous studies we investigated in details the physical properties of the  $\text{Ce}(\text{Ni}_{1-x}\text{Cu}_x)_2\text{Si}_2$  and  $\text{CeNi}_2(\text{Si}_{1-y}\text{Ge}_y)_2$  alloys [5, 8]. We have shown that substitution of Ni for Cu and Ge for Si strongly influences the physical properties of the parent compounds. This work is a continuation of our previous studies on these Ce-based alloys and the effect of the chemical pressure (realized via solid solutions) on the different physical properties [2, 5, 8–12]. However, this time we focus on a parameter determining the usefulness of a material for thermoelectric applications, i.e. the power factor  $PF = S^2/\rho$ , where  $S$  is the Seebeck coefficient and  $\rho$  is the electrical resistivity. Moreover, the use of various substitutions is a well-known strategy for improving the TEP properties of many materials because it introduces multiple scattering centers, which can drive to reduction of the lattice thermal conductivity.

## 2. Experiment details

Sample preparation and structural characterization was described elsewhere [5, 8]. The transport properties of each sample were measured from 2 to 300 K by

use of the thermal transport option (TTO) in a physical properties measurement system (PPMS) by Quantum Design. For selected samples high temperature (up to 1000 K) electrical resistivity and Seebeck coefficient were measured simultaneously using an Linseis LSR-3 instrument system. All measurements were taken on cuboids samples with four-probe measurement technique in a He atmosphere.

## 3. Results and discussions

In Fig. 1 we present electrical resistivity, Seebeck coefficient and  $PF$  in a broad temperature range. The low temperature dependence of the electrical resistivity and Seebeck coefficient are dominated by the Kondo and crystal electric field (CEF) effects. Positive Seebeck coefficient values were obtained for all specimens and increased with an increase in temperature to obtain maximum values at the range from 70 K to 400 K, depending on the chemical composition. High temperature measurements reveal that electrical resistivity becomes more metallic-like and Seebeck coefficient changes sign from positive to negative. All above drives to decrease of the  $PF$  in higher temperatures and  $PF$  values become negligibly small. Therefore, latter we will focus on the low temperature regime.

Figure 2. shows  $\rho$ ,  $S$ , and  $PF$  for La-based alloys. For  $\text{LaNi}_2\text{Si}_2$  our results are consistent with results reported earlier [13, 14]. Because La does not have 4f electrons these alloys show metallic-like behavior in wide temperature range and small values of  $S$  and  $PF$ . It is clearly visible from comparison of  $S(T)$  for  $\text{LaCu}_2\text{Si}_2$  and  $\text{LaNi}_2\text{Si}_2$  (Fig. 2b) that the not-fully occupied 3d states of Ni are responsible for the negative sign of the Seebeck coefficient in  $\text{LaNi}_2\text{Si}_2$ . Hence, the sign change at high temperatures for Ni-rich samples in Fig. 1b results from the

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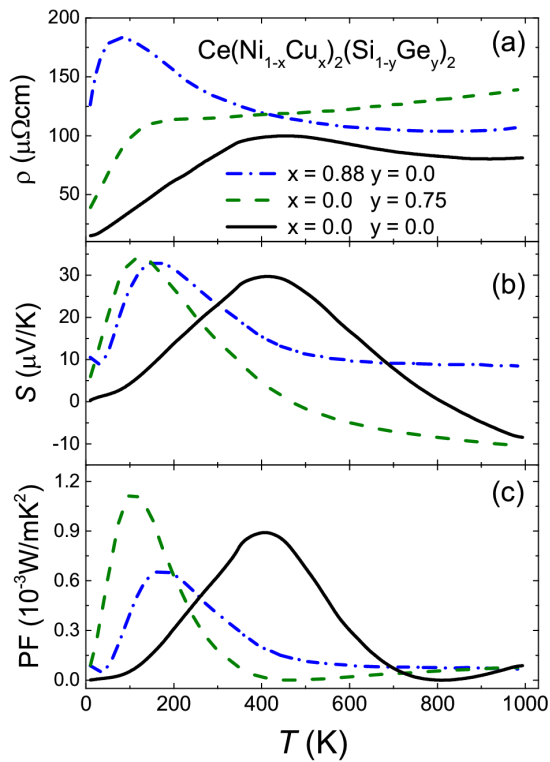


Fig. 1. Temperature dependence of thermoelectric properties for selected  $Ce(Ni_{1-x}Cu_x)_2(Si_{1-y}Ge_y)_2$  alloys, (a) electrical resistivity ( $\rho$ ), (b) Seebeck coefficient ( $S$ ), (c) power factor ( $PF$ ).

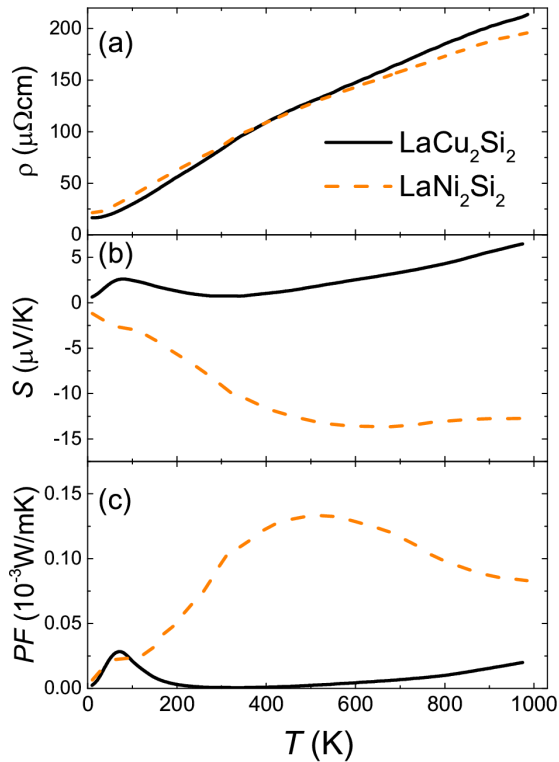


Fig. 2. Temperature dependence of thermoelectric properties for  $La(Ni,Cu)_2Si_2$  alloys, (a) electrical resistivity ( $\rho$ ), (b) Seebeck coefficient ( $S$ ), (c) power factor ( $PF$ ).

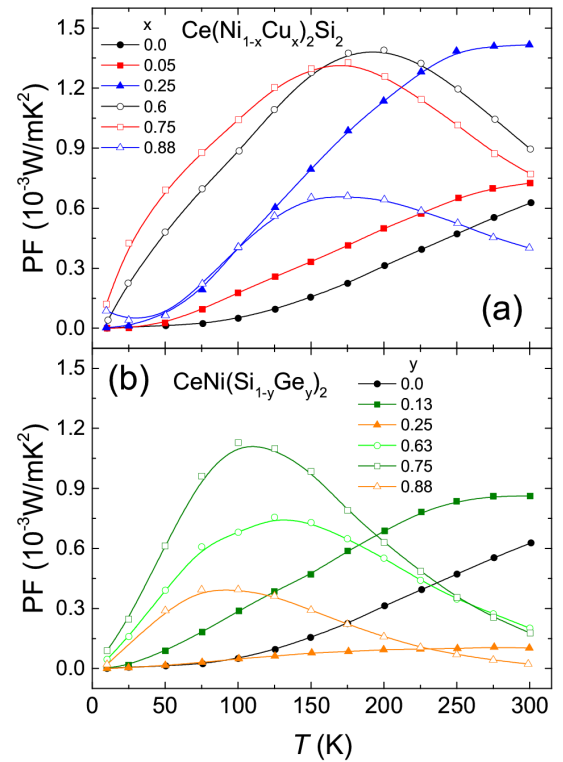


Fig. 3. Power factors in the temperature range 2–300 K for (a)  $Ce(Ni_{1-x}Cu_x)_2Si_2$  and (b)  $CeNi_2(Si_{1-y}Ge_y)_2$  alloys.

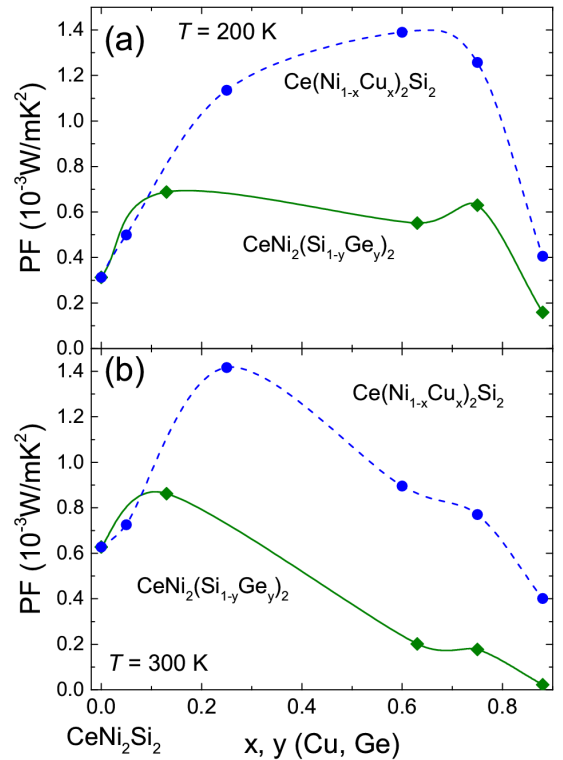


Fig. 4. Composition dependence of power factors for the  $Ce(Ni_{1-x}Cu_x)_2Si_2$  and  $CeNi_2(Si_{1-y}Ge_y)_2$  alloys at (a)  $T = 200$  K and (b) 300 K.

predominance of the Ni contribution at high temperatures enabled by the decrease of the hybridization of the Ce  $f$  states with the conduction electrons.

The thermoelectric  $PF$ s of  $Ce(Ni_{1-x}Cu_x)_2Si_2$  and  $CeNi_2(Si_{1-y}Ge_y)_2$  alloys as a function of temperature are shown in Fig. 3. For all samples  $PF$  shows a broad maximum with both position and value changing sensitively with the concentrations  $x$  and  $y$ .

The  $PF$  is clearly enhanced for middle concentration range (see Fig. 4). For  $Ce(Ni_{1-x}Cu_x)_2Si_2$  system  $PF$  exhibits a maximum value of  $1.4 \times 10^{-3} \text{ Wm}^{-1}\text{K}^{-2}$  at 290 K for  $x = 0.25$ . For the Ge-substituted specimens  $PF$  shows a maximum value of  $1.1 \times 10^{-3} \text{ Wm}^{-1}\text{K}^{-2}$  at 110 K for  $y = 0.75$ . The largest increase in  $PF$  at room temperature can be seen for  $x = 0.25$  with  $PF$  more than twice that of  $CeNi_2Si_2$ . Even greater growth of  $PF$  is observed at 250 K for  $x = 0.6$  and at 100 K for  $y = 0.75$  where the  $PF$  increases almost three and four times, respectively. Figure 4 shows  $PF$  for selected temperatures for all compositions. Compared to other well-known TE materials the obtained  $PF$  values are 10 to 100 times smaller [15]. For example for  $Yb_{0.5}Er_{0.5}Al_3$   $PF = 14.0 \times 10^{-3} \text{ Wm}^{-1}\text{K}^{-2}$  at 200 K [16].

#### 4. Conclusions

The thermoelectric properties of the  $Ce(Ni_{1-x}Cu_x)_2Si_2$  and  $CeNi_2(Si_{1-y}Ge_y)_2$  alloys prepared by arc-melting have been reported.

Power factor shows peak values between 70 K and 400 K, depending on the composition. The largest values of  $PF$  appear usually for middle range of the dopant concentration. At room temperature the maximum value is equal to  $1.4 \times 10^{-3} \text{ Wm}^{-1}\text{K}^{-2}$  for  $Ce(Ni_{0.75}Cu_{0.25})_2Si_2$  and  $0.9 \times 10^{-3} \text{ Wm}^{-1}\text{K}^{-2}$  for  $CeNi_2(Si_{0.87}Ge_{0.13})_2$ . Although the  $PF$  values are improved by substitutions in  $Ce(Ni_{1-x}Cu_x)_2Si_2$  and  $CeNi_2(Si_{1-y}Ge_y)_2$  compared to  $CeNi_2Si_2$ , they are rather too small for applications.

The interpretation of the temperature dependences of the Seebeck coefficient revealed that in the high temperature range it is dominated by the contribution of the Ni  $3d$  states.

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