Low temperature specific heat of superconducting ternary intermetallics La$_3$Pd$_4$Ge$_4$, La$_3$Ni$_4$Si$_4$, and La$_3$Ni$_4$Ge$_4$ with U$_3$Ni$_4$Si$_4$-type structure

S Kasahara, H Fujii, H Takeya, T Mochiku, A D Thakur and K Hirata

Superconducting Materials Center, National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

E-mail: Kasahara.Shigeru@nims.go.jp

Received 24 April 2008, in final form 1 August 2008
Published 21 August 2008
Online at stacks.iop.org/JPhysCM/20/385204

Abstract

A systematic investigation on the thermodynamic properties of La-based ternary intermetallic superconductors crystallizing in a U$_3$Ni$_4$Si$_4$-type structure is presented. The U$_3$Ni$_4$Si$_4$-type structure consists of a characteristic intergrowth of periodic BaAl$_4$ (ThCr$_2$Si$_2$)- and AlB$_2$-type segments. Pristine low temperature specific heat data for recently discovered members La$_3$Ni$_4$Si$_4$ and La$_3$Ni$_4$Ge$_4$ with $T_c$s of 1.0 and 0.7 K, respectively, are presented as well as La$_3$Pd$_4$Ge$_4$ with the highest $T_c$ of 2.5 K in the U$_3$Ni$_4$Si$_4$-type group. Owing to the higher $T_c$s of U$_3$Ni$_4$Si$_4$-type superconductors than the related ThCr$_2$Si$_2$-type compounds, comparisons are drawn in our investigations of the ternary intermetallics of LaPd$_2$Ge$_2$, LaNi$_2$Si$_2$, and LaNi$_2$Ge$_2$ having a ThCr$_2$Si$_2$-type structure. Our investigations of the thermodynamic properties show that La$_3$Ni$_4$Si$_4$ and La$_3$Ni$_4$Ge$_4$ have higher values of $\gamma_n$, $N(E_F)$, and $\Theta_D$ than La$_3$Pd$_4$Ge$_4$. The same trend was found in ThCr$_2$Si$_2$-type compounds of LaPd$_2$Ge$_2$, LaNi$_2$Si$_2$, and LaNi$_2$Ge$_2$. It turns out that the difference in $T_c$ between La$_3$Pd$_4$Ge$_4$, La$_3$Ni$_4$Si$_4$, and La$_3$Ni$_4$Ge$_4$, as well as the relatively higher $T_c$ of the U$_3$Ni$_4$Si$_4$-type superconductors than of the related ThCr$_2$Si$_2$-type compounds, are largely due to the strength of electron–phonon coupling.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Ternary intermetallics with a ThCr$_2$Si$_2$-type structure [1, 2], a BaAl$_4$ derivative, have been studied extensively—especially the issues related to superconductivity and magnetism. A number of compounds crystallize with rare-earth ions, in which the 4$f$ (or 5$f$) electrons hybridize with the conduction electrons and often provide exotic properties. For instance, CeCu$_2$Si$_2$ is the first superconducting material with heavy fermion properties [3]. Compounds crystallizing in the ThCr$_2$Si$_2$-type structure show a rich variety of phenomena related to superconductivity. However, the superconducting critical temperature ($T_c$) in most of such compounds is as low as 1 K, as found for LaPd$_2$Ge$_2$ and LaPt$_2$Ge$_2$ with $T_c$s of 1.12 and 0.55 K [4]$^1$. Meanwhile, significant interest is being generated by the existence of further derivative structures. Among the ThCr$_2$Si$_2$-based derivatives, quaternary intermetallic borocarbides have a derivative structure, interstitially filled by carbon atoms. As represented by the 23 K superconductivity in YPd$_2$B$_2$C, which is the highest found in the ThCr$_2$Si$_2$-type derivatives (see footnote 1), some borocarbides undergo a superconducting transition at moderately high $T_c$, and some of them show unconventional superconductivity [5–9].

Over the past several decades, investigations on various kinds of ThCr$_2$Si$_2$-derivatives have opened up new areas for

$^1$ During the reviewing process, the record of $T_c$ in ThCr$_2$Si$_2$-type intermetallics was broken by the discovery of FeAs-based superconducting materials.
research on superconducting materials. The $U_3Ni_4Si_4$-type structure is also classified in the ThCr$_2$Si$_2$ derivatives with a characteristic periodic intergrowth of BaAl$_4$ (ThCr$_2$Si$_2$) and AlB$_2$-type segments [10]. At present, only about 10 compounds have been found to be ternary $U_3Ni_4Si_4$-type materials [10–21]. Among them, superconductivity has been shown to exist in $La_3Pd_4Ge_4$ and $La_3Pd_4Si_4$ [19, 21]. The $T_c$s of $La_3Pd_4Ge_4$ and $La_3Pd_4Si_4$ (defined by the onset of diamagnetism) are 2.75 and 2.15 K, respectively. In addition, we have recently found superconductivity in two isostructural compounds, $La_3Ni_4Si_4$ and $La_3Ni_4Ge_4$, with $T_c$s of 1.0 and 0.7 K, respectively [22].

Although, the above four compounds having the $U_3Ni_4Si_4$-type structure are found to undergo superconductivity, their detailed thermodynamic properties, as well as the coupling between electrons and phonons, have not been clarified yet. In this work we present the results from our investigations on low temperature specific heat in the $U_3Ni_4Si_4$-type superconductors $La_3Pd_4Ge_4$, $La_3Ni_4Si_4$, and $La_3Ni_4Ge_4$. A related ThCr$_2$Si$_2$-type superconductor, $LaPd_2Ge_2$ [4], and non-superconducting $LaNi_2Si_2$, $LaNi_2Ge_2$, which are the segments of the $U_3Ni_4Si_4$-type compounds [10], are also studied. The Sommerfeld coefficient, $γ_s$, and the Debye temperature, $\Theta_D$, are obtained from the normal state specific heat. Based on the results, the electron–phonon coupling constant, $λ_{ph}$, and the electronic density of states at the Fermi level, $N(E_F)$, are derived for each compound. Our investigations into the thermodynamic properties show that $La_3Ni_4Si_4$ and $La_3Ni_4Ge_4$ have the higher values in $γ_s$, $N(E_F)$, and $\Theta_D$ than $La_3Pd_4Ge_4$. The same trend was found in the related ThCr$_2$Si$_2$-type compounds of $LaPd_2Ge_2$, $LaNi_2Si_2$, and $LaNi_2Ge_2$. It turns out that the differences in $T_c$ between $La_3Pd_4Ge_4$, $La_3Ni_4Si_4$, and $La_3Ni_4Ge_4$ are largely due to the strength of the electron–phonon coupling, while $\Theta_D$ and $N(E_F)$ have less weight on the superconductivity. It is also shown that all the La-based superconductors crystallize in the $U_3Ni_4Si_4$-type structure have higher $λ_{ph}$ than the related ThCr$_2$Si$_2$-type compounds. The superconducting gap in each compound is discussed based on the electronic specific heat, $C_\alpha$, in the superconducting state. We depict a systematic investigation of the thermodynamic and the superconducting properties in the $U_3Ni_4Si_4$- and the related ThCr$_2$Si$_2$-type compounds.

2. Experimental details

We synthesized $La_3Pd_4Ge_4$, $La_3Pd_4Si_4$, $La_3Ni_4Si_4$, and $La_3Ni_4Ge_4$ by the standard arc-melting technique with a stoichiometric ratio of pure elements $La(3N)$, $Pd(4N)$, $Ni(4N)$, Ge(5N), and Si(5N) in an Ar gas atmosphere. The details are described in [19, 21, 22]. The arc-melted buttons were annealed at 900–1100 °C in a vacuum, typically for 1 week. The x-ray diffraction patterns of $La_3Pd_4Ge_4$, $La_3Ni_4Si_4$, and $La_3Ni_4Ge_4$ show that their crystal structure is identical to the $U_3Ni_4Si_4$-type, with a tiny fraction of impurity phases mainly attributed to the ThCr$_2$Si$_2$-type component. The fraction of the impurities in $La_3Pd_4Ge_4$, $La_3Ni_4Si_4$, and $La_3Ni_4Ge_4$ is less than a few per cent. Meanwhile, for $La_3Pd_4Si_4$, it is found to be above 10%, which led us to exclude this compound from the present study. The ThCr$_2$Si$_2$-type compounds of $LaPd_2Ge_2$, $LaNi_2Si_2$, and $LaNi_2Ge_2$ were also synthesized by arc-melting. Single phased samples were obtained for these compounds. Specific heat measurements by the thermal relaxation method were performed in a temperature range from 0.4 to 5.0 K on samples with masses of about 13–28 mg. A platelet shaped polycrystal with polished surfaces is cut from the annealed button, and mounted on a small sapphire chip on which a serpentine metallic heater is evaporated. A Cernox temperature sensor attached to the sapphire chip with gold leads is used to measure the heat capacity. In our system, the level of addenda is 14.0 nJ K$^{-1}$ at 1 K and 0.6 μJ K$^{-1}$ at 5 K, which is independent of the applied field up to 5 T. Precise measurements on the specific heat are carried out by fitting the addenda polynomially and subtracting them.

3. Results and discussion

The main panel of figure 1 shows a plot of specific heat divided by temperature, $C/T$, in $La_3Pd_4Ge_4$, $La_3Ni_4Si_4$, and $La_3Ni_4Ge_4$ as a function of $T^2$, with the inset showing the basic $U_3Ni_4Si_4$-type crystal structure of $La_3Pd_4Ge_4$. Clear specific heat jumps appear in all the samples at temperatures agreeing with the transport data for zero resistivity. The normal state specific heat in each compound is fitted by a linear combination of the electronic contribution $C_\alpha = γ_sT$ and the phonon part $C_{ph} = βT^3 + δT^5$, as drawn by the solid lines. The parameters $γ_s$, $β$, and $δ$, obtained from the data are summarized in table 1. Here, $γ_s = 27.0$ mJ mol$^{-1}$ K$^{-2}$ for $La_3Pd_4Ge_4$, $36.9$ mJ mol$^{-1}$ K$^{-2}$ for $La_3Ni_4Si_4$, and $34.5$ mJ mol$^{-1}$ K$^{-2}$ for $La_3Ni_4Ge_4$, respectively, are obtained. $La_3Pd_4Ge_4$ shows a large $δT^5$ term, suggesting a contribution from complex phonon densities of states. From the relationship $β = (12π^4/5)Nk_B(1/θ_D)^3$, the Debye temperature, $θ_D$, is
estimated as 256 K for La$_3$Pd$_4$Ge$_4$, 321 K for La$_3$Ni$_4$Si$_4$, and 284 K for La$_3$Ni$_4$Ge$_4$. The electron–phonon coupling constant, $\lambda_{ph}$, is calculated by the McMillan formula:

$$T_c = \frac{\Theta_D}{1.45} \exp \left[ \frac{1.04(1 + \lambda_{ph})}{\lambda_{ph} - \mu^* (1 + 0.62\lambda_{ph})} \right],$$

where $\mu^*$ is the Coulomb pseudopotential [23]. Taking a typical value of $\mu^*$ = 0.10–0.13 for metallic materials [23], we obtain $\lambda_{ph} = 0.48–0.55$ for La$_3$Pd$_4$Ge$_4$, 0.39–0.43 for La$_3$Ni$_4$Si$_4$, and 0.38–0.45 for La$_3$Ni$_4$Ge$_4$. The electronic density of states at the Fermi level, $N(E_F)$, is given by the relationship [23]

$$N(E_F) = \frac{4}{\pi^2} k_B^2 (1 + \lambda_{ph}) N(E_F).$$

For the values of $\gamma_s$ and $\lambda_{ph}$ derived above, $N(E_F) = 3.86–3.69$ states/(eV fu) is calculated for La$_3$Pd$_4$Ge$_4$, $N(E_F) = 5.43–5.32$ and 5.16–4.97 states/(eV fu) are derived for La$_3$Ni$_4$Si$_4$ and La$_3$Ni$_4$Ge$_4$, respectively.

The electronic specific heat, $C_e = C - \beta T^3 - \delta T^5$, in the three U$_3$Ni$_4$Si$_4$-type superconductors is shown in figure 2. The main panel shows a plot of $C_e$ vs $T$, and the inset has a plot of $C_e$/$\gamma_s T$ versus $T/T^*$, respectively. Here, $T^*$ denotes the thermodynamic critical temperature considering the entropy balance. As drawn by the solid lines, $C_e$ is fitted by a thermally excited exponential behavior, $C_e \sim \exp(-\Delta_0/k_B T)$, expected for the BCS superconductivity. The superconducting gap, $\Delta_0^{\text{BCS}}$, determined by the experiments is 0.30 meV for La$_3$Pd$_4$Ge$_4$, 0.14 meV for La$_3$Ni$_4$Si$_4$, and 0.09 meV for La$_3$Ni$_4$Ge$_4$. These values are slightly smaller than the theoretical BCS values of $\Delta_0^{\text{BCS}} = 0.33$, 0.16 and 0.12 meV for La$_3$Pd$_4$Ge$_4$, La$_3$Ni$_4$Si$_4$, and La$_3$Ni$_4$Ge$_4$, respectively. For La$_3$Pd$_4$Ge$_4$, the gap $\Delta_0^{\text{exp}}$ gives a value $2\Delta_0^{\text{exp}}/k_BT_c^* \sim 3.08$. The electronic specific heat jump at $T^*$ brings $C_e/\gamma_s T^*$ $\sim 1.24$. For La$_3$Ni$_4$Si$_4$, $2\Delta_0^{\text{exp}}/k_BT_c^* \sim 3.26$ and $C_e/\gamma_s T^*$ $\sim 1.32$ are obtained. These are slightly smaller but comparable with the BCS values of $2\Delta_0^{\text{BCS}}/k_BT_c^* = 3.53$ and $C_e/\gamma_s T^*$ $= 1.43$. Apart from the above two compounds, La$_3$Ni$_4$Ge$_4$ shows smaller values as $2\Delta_0^{\text{exp}}/k_BT_c^* \sim 2.83$ and $C_e/\gamma_s T^*$ $\sim 0.95$. Typically, such a small jump at $T_c$ is observed when the sample includes impurities. However, we have checked that the fraction of impurities in our sample is less than a few per cent and cannot explain the small size of the jump height (≈30% smaller than the BCS value). Growth of single crystalline samples and experiments using them are highly recommended to develop this work further.

For La$_3$Pd$_4$Ge$_4$, the magnetic field dependence of the Sommerfeld coefficient, $\gamma_s(H)$, is also investigated. Figure 3 shows a plot of $\gamma_s(H)$ versus $\mu_0 H$ in La$_3$Pd$_4$Ge$_4$ derived from the field evolution of the specific heat (the inset). The value of $\gamma_s(H)$ is determined by extrapolating the $C/T$ versus $T^2$ curves at $T^2 \leq 0.5$ K$^2$ with the equation $C/T = \gamma_s + \beta_s T^2$. The field dependence of $\gamma_s(H)$ in La$_3$Pd$_4$Ge$_4$ is well fitted by the relationship $\gamma_s(H) = \gamma_s(0) + \gamma_s H/H_d$, which is in marked contrast to the behavior $\gamma_s(H) = \gamma_s(0) + \gamma_s (H/H_d)^{1/2}$ at

| $T_c^0$ (K) | $T^*_c$ (K) | $\gamma_s$ (mJ mol$^{-1}$ K$^{-2}$) | $\beta$ (mJ mol$^{-1}$ K$^{-2}$) | $\delta$ (mJ mol$^{-1}$ K$^{-6}$) | $\Theta_D$ (K) |
|------------|-------------|-------------------------------|-----------------|-----------------|-----------------|
| La$_3$Pd$_4$Ge$_4$ | 2.50 | 2.23 | 27.0 | 1.27 | 12.7 | 256 |
| La$_3$Ni$_4$Si$_4$ | 1.00 | 0.96 | 36.9 | 0.645 | 4.40 | 321 |
| La$_3$Ni$_4$Ge$_4$ | 0.76 | 0.74 | 34.5 | 0.930 | 2.76 | 284 |
| LaPd$_2$Ge$_2$ | 1.10 | 0.96 | 8.26 | 0.393 | 5.05 | 291 |
| La$_3$Ni$_4$Si$_4$ | — | — | 11.3 | 0.208 | 1.97 | 360 |
| La$_3$Ni$_4$Ge$_4$ | — | — | 14.5 | 0.273 | 3.14 | 328 |

*Table 1.* The normal and superconducting parameters of U$_3$Ni$_4$Si$_4$-type La$_3$Pd$_4$Ge$_4$, La$_3$Ni$_4$Si$_4$, La$_3$Ni$_4$Ge$_4$, and ThCr$_2$Si$_2$-type LaPd$_2$Ge$_2$, LaNi$_2$Si$_2$, LaNi$_2$Ge$_2$, derived from the specific heat results.
superconductivity in the latter two [4, 27]. Owing to the relatively higher $T_c$ of LaNi$_2$Si$_2$ and LaNi$_2$Ge$_2$. In LaNi$_2$Ge$_2$, $\gamma_c(0) = \mu_0 H_c(0)$ is in good agreement with the conventional BCS superconductor with an isotropic gap.

Figures 3 and 4. Magnetic field dependence of the Sommerfeld coefficient in the superconducting state, $\gamma_s(H)$, defined by extrapolating the C/T versus $T^2$ plot (the inset) at $T^2 \leq 0.5$ K$^2$. The solid line shows the function $\gamma_s(H) = \gamma_s(0) + \mu_0 H_c(0)$. The field dependence of $\gamma_s(H)$ is in good agreement with the conventional BCS superconductor with an isotropic gap.

$H \ll H\!\!\!\!_c$, expected for nodal superconductors [8, 24]. As well as the exponential behavior of the $C/T$ in figure 2, $\gamma_s(H) \propto H$ shows that La$_3$Pd$_4$Ge$_4$ is a fully gapped superconductor, in which $\gamma_s(H)$ is proportional to the density of vertices, carrying a zero energy density of states. It should also be noted that the value of $\mu_0 H\!\!\!\!_c \sim 0.4$ T is in good agreement with our earlier results determined by the linear extrapolation of the $H\!\!\!\!_c(T)$ curve obtained from magnetization measurements [19]. In addition, the validity of the present experiments is also confirmed by deducing the thermodynamic critical field, $\mu_0 H_c(0)$, from the specific heat data. According to the BCS prediction, the zero temperature value of the thermodynamic critical field, $\mu_0 H_c(0)$, is given by the following relationship:

$$\mu_0 V_m H_c(0)^2 = 0.47 \gamma_s T_c^2$$

where $V_m$ represents the molar volume. By taking the lattice parameters $a = 4.2293(1)$ Å, $b = 4.3823(1)$ Å, and $c = 25.0109(8)$ Å [20] as well as the derived values of $\gamma_s$ and $T_c$, $\mu_0 H_c(0) = 23.8$ mT is obtained. This is close to the value of $\mu_0 H_c(0) = 28$ mT [19] derived from $\mu_0 H_c(0) = \mu_0 H_{\mathrm{WHH}}^c(0)/\sqrt{2\kappa(0)}$, where $\kappa(0)$ denotes the Ginsburg–Landau parameter and $H_{\mathrm{WHH}}^c(0) = 0.69 T_c(dH_c/dT)_c$, the upper critical field defined by the Werthamer–Helfand–Hohenberg (WHH) formula [25, 26].

According to the past works, all the U$_3$Ni$_4$Si$_4$-type superconductors based on lanthanum exhibit higher $T_c$'s than the related compounds having the ThCr$_2$Si$_2$-type structure, i.e. LaPd$_2$Ge$_2$, LaPd$_2$Si$_2$, LaNi$_2$Ge$_2$, and LaNi$_2$Si$_2$ with $T_c \sim 1.17$, 0.39 K for the two former compounds and no superconductivity in the latter two [4, 27]. Owing to the relatively higher $T_c$ of U$_3$Ni$_4$Si$_4$-type superconductors, we also studied the thermodynamic properties in LaPd$_2$Ge$_2$, LaNi$_2$Si$_2$, and LaNi$_2$Ge$_2$ as reference compounds, which are considered as the segments of La$_3$Pd$_4$Ge$_4$, La$_3$Ni$_4$Si$_4$, and La$_3$Ni$_4$Ge$_4$.

Figure 4 shows a plot of C/T versus $T^2$ in LaPd$_2$Ge$_2$, LaNi$_2$Si$_2$, and LaNi$_2$Ge$_2$. In LaNi$_2$Si$_2$ and LaNi$_2$Ge$_2$, C/T–$T^2$ curves show up-turns at low temperatures, which are fitted by the Schottky-type anomaly for a two-level system with energy difference $\delta \sim 1.18$ K, presumably arising from the crystalline electric field splitting of the Ni d-electron orbital. Following the same analysis on the normal state specific heat, $\gamma_n = 8.26$ mJ mol$^{-1}$ K$^{-2}$, $\beta = 0.393$ mJ mol$^{-1}$ K$^{-4}$, and $\delta = 5.06$ mJ mol$^{-1}$ K$^{-6}$ are obtained for LaPd$_2$Ge$_2$. On the other hand, by fitting the data at $T > 2.5$ K, $\gamma = 11.3$ mJ mol$^{-1}$ K$^{-2}$, $\beta = 0.208$ mJ mol$^{-1}$ K$^{-4}$, $\delta = 1.97$ mJ mol$^{-1}$ K$^{-6}$ and $\gamma = 14.5$ mJ mol$^{-1}$ K$^{-2}$, $\beta = 0.273$ mJ mol$^{-1}$ K$^{-4}$, $\delta = 3.14$ mJ mol$^{-1}$ K$^{-6}$ are obtained for LaNi$_2$Si$_2$ and LaNi$_2$Ge$_2$, respectively. $\Theta_B$ is calculated as 291 K for LaPd$_2$Ge$_2$, 360 K for LaNi$_2$Si$_2$, and 328 K for LaNi$_2$Ge$_2$. The electron–phonon coupling constant in LaPd$_2$Ge$_2$ is calculated as $\lambda_{ph} = 0.39–0.45$ for $\mu^* = 0.10–0.13$. For LaNi$_2$Si$_2$ and LaNi$_2$Ge$_2$, the absence of superconductivity, at least down to 320 mK, suggests $\lambda_{ph} < 0.33–0.38$ in these compounds. $N(E_F)$ in LaPd$_2$Ge$_2$ is derived as 1.69–1.63 states/(eV f.u.) for the values $\gamma_n = 8.26$ mJ mol$^{-1}$ K$^{-2}$ and $\lambda_{ph} = 0.39–0.45$. On the other hand, $N(E_F) = 2.33$ and 2.91 states/(eV f.u.) are given for LaNi$_2$Si$_2$ and LaNi$_2$Ge$_2$ in the limit of $\lambda_{ph} \rightarrow 0$. The electronic specific heat, $C_{el}$, for LaPd$_2$Ge$_2$ is analyzed in the inset of figure 4. In the superconducting state of LaPd$_2$Ge$_2$, $C_{el}$ is fitted by the BCS model, yielding values of $\Delta C_{el}/\gamma_s T_c^2 = 0.05$ and $\Delta/\gamma_s T_c^2 = 3.65$.

In the following, we compare the thermodynamic and superconducting properties of La$_3$Pd$_4$Ge$_4$, La$_3$Ni$_4$Si$_4$, and La$_3$Ni$_4$Ge$_4$, and also LaPd$_2$Ge$_2$, LaNi$_2$Ge$_2$, and LaNi$_2$Si$_2$. All the parameters obtained in the present experiments are summarized in table 1. According to the simple BCS model, a high electronic density of states at the Fermi level, Debye temperature, and strong electron–phonon coupling will bring higher $T_c$, as it is given as $T_c = 1.33\Theta_B\exp[-1/(E_F V)]$, where $V$ is the strength of the electron–phonon interaction. Looking over the other ThCr$_2$Si$_2$-type derivatives, quaternary
less than half of those in La3Pd4Ge4. Judging from the superconductors, La3Ni4Si4 shows the highest values in La3Ni4Ge4. On the other hand, La3Pd4Ge4 shows the and LaPd2Ge2 are all of the conventional BCS-type. This structure calculations are also needed.

measurements should be confirmed by other experimental phonon coupling investigated by the present thermodynamic analyses based on the specific heat measurements, the difference in the T_vs in La3Pd4Ge4, La3Ni4Ge4, and La3Ni4Si4 is attributed to the strength of the electron–phonon coupling. In contrast to the smaller values of \(\gamma_s\) and \(N(E_F)\), and \(\Theta_D\), La3Pd4Ge4 has about 20% larger \(\lambda_{ph}\) than the other U3Ni4Si4-type superconductors. It should also be noted that such a trend of the electron–phonon coupling is also found in the ThCr2Si2-type compounds. Looking at the parameters in La3Pd4Ge4, La3Ni4Si2, and La3Ni4Ge2 again, \(\Theta_D\) and \(N(E_F)\) appear to have less weight on the T_vs in these compounds. Instead, \(\lambda_{ph} = 0.39\)–0.45 for La3Pd4Ge4, together with \(\lambda_{ph} < 0.33\)–0.38 for La3Ni4Si2 and La3Ni4Ge2, suggesting that the differences in \(T_c\) in these three ThCr2Si2-type compounds are mainly due to differences in \(\lambda_{ph}\). Moreover, differences in \(\lambda_{ph}\) are also found between the U3Ni4Si4- and ThCr2Si2-type compounds. Our thermodynamic investigations show that all the U3Ni4Si4-type superconductors based on lanthanum have larger \(\lambda_{ph}\) than the ThCr2Si2-type compounds, while \(T_c\) is less dependent on \(\Theta_D\) or \(N(E_F)\). In figure 5, the relationship between \(T_c^\text{th}\) and \(\lambda_{ph}\) (derived for \(\mu^* = 0.13\)) in the U3Ni4Si4- and the ThCr2Si2-type compounds are summarized. Black closed circles are the data from the specific heat results. For La3Ni4Si2 and La3Ni4Ge2, an indistinct spot at \(\lambda_{ph} \leq 0.38\) shows the expected positions of \(T_c^\text{th}\) versus \(\lambda_{ph}\) if these compounds show superconductivity below 320 mK. On the other hand, those for La3Pd4Si4 and La3Pd4Si3 are deduced by considering the T_vs of these compounds. \(T_c^\text{th}\) s in the U3Ni4Si4- and ThCr2Si2-type compounds appear to be universally dependent on \(\lambda_{ph}\). For a more elaborated understanding, the role of the electron–phonon coupling investigated by the present thermodynamic measurements should be confirmed by other experimental techniques such as Raman spectroscopy, etc. Detailed band structure calculations are also needed.

Finally, let us comment on a potential of the intermetallic compounds crystallized in the U3Ni4Si4-type structure. Concerning the nature of the gap symmetry, the present experiments revealed that La3Pd4Ge4, La3Ni4Si2, La3Ni4Ge4, and La3Pd4Ge2 are all of the conventional BCS-type. This is rationalized considering the fact that lanthanum does not have 4f electrons and no hybridization occurs between the conduction electrons. If the lanthanum in the U3Ni4Si4-type structure can be substituted for the other rare-earths, it may bring some exotic properties to the superconducting state, as have been investigated in a number of ThCr2Si2 derivatives. So far, most of the rare-earth substitutions are reported to fail to stabilize the U3Ni4Si4-type structure. Alternatively, compounds with Gd3Cu4Ge4-type structure, such as Ln3Pd4Ge4 (Ln = Y, Gd, Tb, Dy, Ho, Er, Tm, and Yb) [28–33] are synthesized. In these compounds, cages of Pd–Ge are formed instead of the Pd–Ge networks in La3Pd4Ge4. By contrast, substitution of the lanthanum by cerium is reported to succeed in synthesizing Ce3Pd4Ge4, crystallizing in the U3Ni4Si4-type structure with Kondo lattice properties [14]. Since these U3Ni4Si4- and Gd3Cu4Ge4-type compounds are candidates for the various ground states governed by competition between the RKKY and Kondo interactions, more investigation is urgently needed on the possibility of novel phenomena related to the superconductivity and magnetism. Single crystal growth of U3Ni4Si4-type compounds will also open up a new area for investigations.

4. Summary

To summarize, we have presented a systematic investigation on the thermodynamic properties in ternary U3Ni4Si4-type intermetallic superconductors La3Pd4Ge4, La3Ni4Si4, and La3Ni4Ge4, and ThCr2Si2-type LaPd2Ge2, LaNi2Si2, and LaNi2Ge2. From the normal state specific heat, the Sommerfeld coefficient, \(\gamma_s\), the Debye temperature, \(\Theta_D\), and the electronic density of states at the Fermi level, \(N(E_F)\), are estimated. The electronic specific heat in each of these compounds showed thermally excited exponential behavior in the superconducting state. In La3Pd4Ge4, the Sommerfeld coefficient in the superconducting state, \(\gamma_s\), showed linear field dependence. These results suggest that La3Pd4Ge4, La3Ni4Si4, La3Ni4Ge4, and La3Pd4Ge2 are superconductors with isotropic gaps. Although, La3Ni4Si2 and La3Ni4Ge4 show higher \(N(E_F)\) than La3Pd4Ge4, presumably contributed by the Ni 3d band, their \(T_c\)s are lower than that of La3Pd4Ge4. The present investigations on the specific heat suggest that this is due to differences in the electron–phonon coupling. The electron–phonon coupling constant, \(\lambda_{ph}\), in La3Pd4Ge4
is larger than those in La₃Ni₄Si₄ and La₃Ni₄Ge₄. The same relationship was found for ThCr₂Si₂-type LaPd₂Ge₂, LaNi₂Si₂, and LaNi₂Ge₂. Additionally, the U₃Ni₄Si₄-type La₃Pd₄Ge₄, La₃Ni₄Si₄, and La₃Ni₄Ge₄ showed higher λₚ than the corresponding ThCr₂Si₂-type LaPd₂Ge₂, LaNi₂Si₂, and LaNi₂Ge₂. The role of the electron–phonon coupling investigated with the present thermodynamic measurements should also be confirmed using other experimental techniques.

Acknowledgments

The authors thank Dr I Hase at AIST and Dr M Imai at NIMS for fruitful discussions. SK is supported by a Grant-in-Aid Scientific Research for Young Scientists (B), from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

References

[1] Ban Z and Sikirica M 1965 Acta Crystallogr. 18 594
[2] Just G and Pautler P 1996 J. Alloys Compounds 232 1
[3] Steglich F, Aarts J, Bredl C D, Lieke W, Meschede D, Franz W and Schafer H 1979 Phys. Rev. Lett. 43 1892
[4] Hull G W, Wernick J H, Geballe T H, Waszczak J V and Bernardini J E 1981 Phys. Rev. B 24 6715
[5] Cava R J, Takagi H, Batlogg B, Zandbergen H W, Krajewski J J, Peck W F Jr, van Dover R B, Felder R J, Siegrist T, Mizahashi K, Lee J O, Eisaki H, Carter S A and Uchida S 1994 Nature 367 146
[6] Cava R J, Takagi H, Zandbergen H W, Krajewski J J, Peck W F Jr, Siegrist T, Batlogg B, van Dover R B, Felder R J, Mizahashi K, Lee J O, Eisaki H and Uchida S 1994 Nature 367 252
[7] Cava R J, Batlogg B, Siegrist T, Krajewski J J, Peck W F Jr, Carter S, Felder R J, Takagi H and van Dover R B 1994 Phys. Rev. B 49 12384
[8] Nohara M, Isshiki M, Takagi H and Cava R J 1997 J. Phys. Soc. Japan 66 1888
[9] Muller K H and Narozhnyi V N 2001 Rep. Prog. Phys. 64 943
[10] Yarmolyuk J P, Akselrud J G, Grin Yu N, Fundamenskii V S and Gladyshevski E I 1979 Sov. Phys.—Crystallogr. 24 332
[11] Hovestreydt E, Klipp K and Parthe E 1982 Acta Crystallogr. B 38 1803
[12] Parthe E, Chabot B, Braun H F and Engel N 1983 Acta Crystallogr. B 39 588
[13] Rogl P, Chevalier B and Etourneau J 1990 J. Solid State Chem. 88 429
[14] Im H J, Kwona Y S and Jung M H 2002 Solid State Commun. 124 181
[15] Chevalier B and Etourneau J 1999 J. Magn. Magn. Mater. 196/197 880
[16] Kuang J P, Cui H J, Li J Y, Yang F M, Nakotte H, Brick E and de Boer F R 1992 J. Magn. Magn. Mater. 104 1475
[17] Kaczorowski D, Noel H and Potel M 1995 Physica B 206/207 457
[18] Pechev S, Chevalier B, Laargue D, Darriet B, Roisnel T and Etourneau J 1999 J. Magn. Magn. Mater. 191 282
[19] Fujii H, Mochiku T, Takeya H and Sato A 2005 Phys. Rev. B 72 214520
[20] Mochiku T, Fujii H, Takeya H, Wuernisha T, Mori K, Ishigaki T, Kamiyama T and Hirata K 2007 Physica C 463–465 182
[21] Fujii H 2006 J. Phys.: Condens. Matter 18 8037
[22] Fujii H and Kasahara S 2008 J. Phys.: Condens. Matter 20 075202
[23] McMillan W L 1968 Phys. Rev. 167 331
[24] Volovik G E 1993 JETP Lett. 58 469
[25] Helfand E and Werthamer W R 1966 Phys. Rev. 147 288
[26] Werthamer N R, Helfand E and Hohenberg P C 1966 Phys. Rev. 147 295
[27] Palstra T T M, Lu G, Menovsky A A, Nieuwenhuys G J, Kes P H and Mydosh J A 1986 Phys. Rev. B 34 4566
[28] Rieger W 1970 Monatsch. Chem. 101 449
[29] Liebrich O, Schafer H and Weiss A 1970 Z. Naturf. B 25 650
[30] Gladyshevskii R E, Sologub O L and Parthe E 1991 J. Alloys Compounds 176 329
[31] Prots’ Yu M, Bodak O I, Pecharsky V K, Salamakha P S and Seropegin Yu D 1993 Z. Kristallogr. 205 331
[32] Salamakha P, Sologub O, Yakintos J K and Routsi Ch D 1998 J. Alloys Compounds 267 192
[33] Niepmann D, Prots’ Y M, Potrgen R and Jeitschko W 2000 J. Solid State Chem. 154 329