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Crystal structure and physical properties of LaPd₂Ge and a novel compound LaPdGe₃



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ABSTRACT

The crystal structures of LaPd₂Ge and LaPdGe₃ have been refined by X-ray diffraction on powdered polycrystalline samples. These ternaries crystallize in YPd₂Si (*Pnma*) and BaNiSn₃ (*I4mm*) structure types, respectively. As revealed by electrical resistivity, thermoelectric power and specific heat measurements, the former compound is superconducting below 0.6 K, which is not the case for the latter one (at least down to 0.3 K). Moreover, LaPdGe₃ was found to be a typical metal in comparison to LaPd₂Ge which is rather a semimetal.

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1. Introduction

Among numerous ternary La-based silicides and germanides, containing transition metal T, superconductivity is often encountered at rather low temperatures. Most of them have crystal structures which are mainly derived from that of BaAl₄ type (space group (s.g.) I4/mmm) [1], such as the tetragonal BaNiSn₃-, ThCr₂Si₂or CaBe₂Ge₂-types and related orthorhombic U₂Co₃Si₅-type (s.g. *Ibam*). However, La₂Pd₃(Si and Ge)₅, adopting the latter structure have not been reported to be superconducting [2]. All these structures are characterized by the stacking of $[La_4(T;M)_4]$ antiprismatic structure elements, where M = Si or Ge. For example, representatives of the tetragonal BaNiSn₃ group are LaRhSi₃ or LaIrSi₃ [3] and LaPdSi₃ [2] which become superconducting with the transition temperature T_c = 1.9, 2.7 and 2.6 K, respectively. These compounds have attracted some interest since their structure lacks the mirror plane normal to the *c*-axis as is the case of superconducting heavyfermion silicide, CePt₃Si, crystallizing in the tetragonal CePt₃B-type structure (s.g. P4mm) [4]. Thus such a situation where a system is without inversion symmetry may lead to a possible admixture of spin-singlet and triplet pairings [5]. There are also many superconductors having the ThCr₂Si₂-type structure, as it is sufficiently here to mention e.g. $LaPd_2Ge_2$ ($T_c = 1.12$ K) and $LaPt_2Ge_2$ ($T_c = 0.55$ K) [6]. Some structure correlations between the superconducting

LaRh₂Si₂, La₂Rh₃Si₅ and La(Rh;Ir)Si₃ have been established by Lejay et al. [3]. Thus, these authors claim that the presence in these ternaries of monocaped square antiprisms as $[(La_4Si_4)Si]$, $[(La_4Si_4)T]$ and $[(La_4T_4)Si]$ configurations, where T = Rh or Ir, favor the occurrence of superconductivity in this kind of materials.

Another tetragonal group of La-based silicides and germanides is that adopting the U₃Ni₄Si₄-type structure (s.g. Immm) consisting of the combination of structural units of AlB₂-type and BaAl₄-type [7]. The highest T_c of 2.75 K in this group of ternaries is just exhibited by La₃Pd₄Ge₄ [8,9]. Interestingly that the isotypic silicide, $La_3Pd_4Si_4$, is also superconducting but with lower T_c of 2.15 K [10]. Electronic structures of these superconducting ternaries have been calculated within the density functional theory [11]. It was found that the computed Fermi surfaces (FSs), originating from several bands, contain both hole-like and electron-like sheets, possessing different dimensionality, in particular quasi twodimensional cylinders with nesting properties that underline the phonon mechanism of their superconductivity. It turned out that densities of states at the Fermi energy are inversely proportional to the T_c 's which allowed to classify them as strongly coupled electron-phonon superconductors. A similarly high temperature T_c to that in La₃Pd₄Ge₄ was found in the case of an alloy having chemical composition LaPd_{0.6}Ge_{1.4}, thought its isostructural counterpart LaPd_{0.5}Si_{1.5} is non-superconducting. Both these allovs crystallize in a favorable for superconductivity crystal structure, namely in the AlB₂-type [2]. Finally, among the La–Pd–*M* systems, there exists LaPd₂Ge, adopting the orthorhombic crystal structure







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Fig. 1. Experimental powder (red) and calculated (black) X-ray diffraction patterns for LaPd₂Ge (a) and LaPdGe₃ (b) in Rietveld refinement. On the bottom the difference curves (blue) are shown. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

of the YPd₂Si-type. This type of structure is described as an ordered derivative of the Fe₃C type, s.g. *Pnma*, *Z* = 4, [12,13]. No report exists about structure and physical properties for such a silicide. This 1:2:1 germanide showed the superconductivity around 0.6 K in the resistivity measurement, but without any sign in the specific heat measurement at this temperature [2]. The authors of this paper have concluded that the observed resistivity anomaly was not intrinsic, but due to an unknown impurity phase.

In this paper we synthesized LaPd₂Ge and carried out its crystal structure refinement. Based on the low temperature specific heat and thermoelectric power results, we present here respective proves of superconducting properties of this material. We also present here the refined structure and physical properties of LaP-dGe₃ phase being not studied before.

2. Experimental details

The polycrystalline samples of LaPd₂Ge and LaPdGe₃ were synthesized by arc melting the constituent elements in a stoichiometric ratio under argon gas atmosphere. Starting materials were La chunks (3N), Pd sheets (4N) and Ge granule (5N). The melting was repeated several times. The weight loss was less than 1%. The obtained button wrapped in a Mo foil was annealed in an evacuated tube at 730 °C for three weeks and then they were examined by X-ray powder diffraction (XRD). Data were collected at room temperature employing a STOE STADI P diffractometer with a linear PSD and Cu K α_1 radiation ($\lambda = 0.15406$ nm). The lattice parameters were calculated using the STOE WinXPow program [14]. Structure refinement was performed using the Rietveld method implemented in the FULLPROF program [15,16], employing internal tables for X-ray atomic form factors. Atom parameters were standardized with the aid of the program STRUCTURE TIDY [17]. In both structures the occupation parameters for the each site were refined separately and found to be very close to 1.0. Then it has been fixed at that meaning, except Ge1 site in LaPdGe3 structure for which the slight disorder due to partial occupation with Ge atoms was detected.

For electrical resistivity measurements the samples in the form of pillars (barshaped) were cut from an annealed bulk material with the dimension of about $5 \times (0.4 - 0.6) \times (0.3 - 0.4)$ mm³. The electrical contacts (four points) were carried out by the electrochemical deposition of Cu and finally silver thin wires were glued by using a silver paste. The measurements were carried out in a ³He cryostat in the temperature range 0.3–300 K, using a four point AC method. A homemade set-up [18] was used for the thermoelectric power measurements at temperatures from 0.3 to 300 K. The frontal surfaces of samples with dimensions of about $2.8 \times 0.4 \times 0.3$ mm³ were wetted with the liquid In–Ga alloy in order to improve the thermal and electrical contacts with chamber plates. The specific heat of the LaPd₂Ge and LaPdGe₃ samples with masses of 16.5 and 7.8 mg, respectively was measured by thermal relaxation method in a commercial Quantum Design PPMS platform in the temperature range 0.4–16 K and in magnetic fields of 0 and 9 T.

3. Results and discussion

3.1. Crystal structure refinement

The powder X-ray spectra of LaPd₂Ge and LaPdGe₃ could be indexed on the basis of orthorhombic and tetragonal unit cells, respectively. Fig. 1a illustrates the experimental X-ray powder pattern for the former germanide that despite the long term exposure of 60 sec/point presents high background and weak intensity reflexes. Taking into account that most of the other germanides from the La-Pd-Ge ternary systems (LaPdGe₃, La₃Pd₄Ge₄, La₂PdGe₆, LaPd₂Ge₂) produce usually the high quality patterns, one can conclude that if they are present as the secondary phases in the studied material their reflexes should be easy observed, but this is not the case. On the contrary, the presence of LaPd₂Ge cannot be easy detected by this method on the X-ray powder pattern of LaPdGe₃ due to the bad X-ray scattering effect of this 1:2:1 germanide. In turn, according to Fig. 1b on the X-ray diagram of LaPdGe₃ some trace of the unknown phase is really present but no reflexes of LaPd₂Ge are observed. Nevertheless, as we will indicate below, it is probable that the 1:1:3 alloy contains the latter phase in some trace amount but being not detected by X-ray scattering. The lattice, positional and thermal parameters determined at room temperature for both these compounds are given in Tables 1a, 1b, 2a and 2b, respectively.

Jorda et al. [13] were first to report LaPd₂Ge to be isotypic with YPd₂Si. The unit cell of LaPd₂Ge with its peculiarities is given in Fig. 2. Our lattice parameters are approximately the same as the values given previously [2]. Up to now except for prototype YPd₂Si, the position parameters of this type structure have been given for CePd₂Ga [19], Yb(Pd;Pt)₂Si [20] and ErPd₂M(Si;Ge) [21] based on the X-ray single crystal and powder diffraction experimental data. In the LaPd₂Ge structure the La atoms are located inside low symmetry polyhedra with 19 apexes [4La + 10Pd + 5Ge], Pd atoms are coordinated with 11 atoms [4La + 4Pd + 3Ge], whereas the coordination polyhedra of the Ge atoms are the distorted trigonal prisms with three additional Pd atoms [(3La + 3Pd)+3Pd]. In order to describe the atomic order in the LaPd₂Ge structure one can use the nearest environment of the La atom (up to 0.34 nm) including only 11 atoms instead 19, which this time form a strongly distorted pentagonal antiprism with one additional atom [(8Pd + 2Ge) + 1Ge] (Fig. 2a). Along the *a*-axis the neighboring pentagonal

 Table 1a
 Crystallographic and structure refinement parameters for LaPd2Ge.

Space group	Pnma
Prototype	YPd ₂ Si
Composition from refinement (at.%)	La ₂₅ Pd ₅₀ G ₂₅
Cell dimensions (nm)	
а	0.76875(4)
b	0.69543(3)
С	0.58099(3)
Cell volume, V (nm ³)	0.31060(4)
Reflections measured	160
Θ range	$10\leqslant 2arrow\leqslant 90$
Number of variables	20
$R_{\rm F} = \Sigma F_{\rm o} - F_{\rm c} / \Sigma F_{\rm o}$	0.056
$R_{\rm I} = \Sigma I_{\rm o} - I_{\rm c} / \Sigma I_{\rm o}$	0.072
$R_{\rm wP} = [\Sigma w_{\rm i} y_{\rm oi} - y_{\rm ci} ^2 / \Sigma w_{\rm i} y_{\rm oi} ^2]^{\frac{1}{2}}$	0.103
$R_{\rm wP} = [\Sigma w_{\rm i} y_{\rm oi} - y_{\rm ci} ^2 / \Sigma w_{\rm i} y_{\rm oi} ^2]^{\frac{1}{2}}$	0.079
$R_{\rm e} = [(N - P + C) / \Sigma w_{\rm i} y_{\rm oi}^2)]^{\frac{1}{2}}$	0.054
$\chi^2 = (R_{\rm wP}/R_{\rm e})^2$	3.60

antiprisms combine via common pentagonal faces producing the infinite zigzag-like pentagonal channels in which the La atoms are located (Fig. 2b). The neighboring channels share apexes and edges (Fig. 2c), so as all the atoms in the crystal are taken into consideration, and no other spacing element can be inserted. It is remarkable that the 3D crystal space can also be fully filled using only all the Ge atoms and their polyhedra. Otherwise is the case of the Pd atoms, not for all of them their polyhedra are needed to describe the structure. In the present paper we use the truncated polyhedra of the La atoms because just their environment become the most important in determination of physical properties of the studied material.

It should be noted that LaPdGe₃ is a new representative of the BaNiSn₃ type structure. For example, a large number of the CeTM₃ compounds crystallize in this type of structure, characterized by s.g. *I4mm*. In this structure three Wyckoff positions 2*a*, are orderly occupied by all three kinds of atoms, La, Pd and Ge2, respectively, while an inequivalent Ge1 atom takes the 4*b* position (Table 2b). Our position parameters determined for LaPdGe₃ from the X-ray powder diffraction data using Rietveld refinement procedure are close to those e.g. for CeT(Si,Ge)₃ (*T* = Ru, Rh, Ir) found in single-crystalline X-ray diffraction experiments [22].

As mentioned above in both studied here germanides their Xray powder diffractions test a small fraction of impurity phases being less than a few percent.

3.2. Physical properties

The electrical resistivity, ρ , as a function of temperature for LaPd₂Ge and LaPdGe₃ is given in Fig. 3. As seen, for both these ternaries the resistivity decreases with a small negative curvature with decreasing temperature down to about 50 K, but below it starts to saturate to some small value of residual resistivity, ρ_0 , extrapolated to T = 0 K. The overall temperature behavior of the resistivity, $\rho(T)$, for both these compounds, being typical of metallic-type conductivity, was then fitted to the generalized relation, Eq. (1) [23]:

$$\rho(T) = \rho_0 + \rho_{BG}(T) + KT^3, \tag{1}$$

where the second term is given by the Bloch-Grünaissen (BG) relation (Eq. (2)):

Table 2a

Crystallographic and structure refinement parameters for LaPdGe₃.

Space group	I 4 mm
Prototype	BaNiSna
Composition from refinement. (atoms per	LapPd2Ge11 se
unit cell)	$Ge2_4 \equiv La_2Pd_2Ge_{5.96}$
Cell dimensions. (nm)	
a	0.450790(8)
с	0.98478(2)
Cell Volume, $V(nm^3)$	0.200120(4)
Reflections measured	52
Θ range	$10 \leq 2\Theta \leq 112$
Number of variables	57
$R_{\rm F} = \Sigma F_{\rm o} - F_{\rm c} / \Sigma F_{\rm o}$	0.071
$R_{\rm I} = \Sigma I_{\rm O} - I_{\rm c} / \Sigma I_{\rm O}$	0.080
$R_{\rm wP} = [\Sigma w_{\rm i} y_{\rm oi} - y_{\rm ci} ^2 / \Sigma w_{\rm i} y_{\rm oi} ^2]^{1/2}$	0.092
$R_{\rm P} = \Sigma y_{\rm oi} - y_{\rm ci} / \Sigma y_{\rm oi} $	0.072
$R_{e} = \left[(N - P + C) / \sum w_{i} y_{ci}^{2} \right]^{1/2}$	0.048
$\chi^2 = (R_{\rm wP}/R_{\rm e})^2$	3.65

$$\rho_{\rm BG}(T) = a(T/\Theta_{\rm D}^{\rm R})^n \int_0^{\Theta/T} \frac{z^n {\rm d} z}{(e^z - 1)(1 - e^{-z})},\tag{2}$$

while the third term is the additional Mott interband scattering *s*-*d* term. The parameters *a* and Θ_D^R in Eq. (2) are the constant and the Debye temperature, respectively. The obtained respective values a, Θ_D^R and *K*, when keeping *n* = 3, are given in Table 3 compared to those found previously for La₂PdGe₆ [24].

As Fig. 3 indicates, good overall fits of experimental data to Eq. (1) were found up to RT (see the black dashed lines) for the studied here germanides. Although all these terms yield the similar T variation of the resistivity for both compounds, the absolute resistivity values at RT of LaPd₂Ge and LaPdGe₃ are about one order of magnitude different. The comparison in $\rho(T)$ of these two compounds is shown in the left hand inset of this figure. If the former germanide behaves as many nonmagnetic intermetallic reference compounds given in the literature (see e.g. $\rho(T)$ for LaPd_{0.5}Si_{1.5} [2] and La₃Pd₄Ge₄ [8]), the latter germanide behaves just as a good metallic material. The RT and residual resistivities for LaPd₂Ge and LaPdGe₃ are approximately 240 and 15.5 $\mu\Omega$ cm compared to 30 and 0.53 $\mu\Omega$ cm, respectively. In turn, the low temperature behaviors for these two germanides are shown in the respective insets to Fig. 3. No doubt that the resistivity of LaPd₂Ge reaches zero resistance at 0.6 K, as it has been reported earlier in Ref. [2]. However, the authors of the cited paper treated this result as a presence of unknown impurities due to the lack of any distinct anomaly in the specific heat, C_p . We will show below, however, that LaPd₂Ge is actually a superconductor with $T_c \approx 0.6$ K. On the other hand, LaPdGe₃ though exhibits a similar jump in the resistivity at the same temperature as the 1:2:1 germanide, its ρ however does not go to zero, and no anomaly in that temperature region is seen in $C_p(T)$, as indicated below. This jump is probably caused just by the presence of LaPd₂Ge impurity though this fact does not confirm directly the X-ray analysis discussed above. It is well-known that the presence of even 3–5% of superconducting impurities gives a strong effect on the low-temperature resistivity.

Surprisingly that the isostructural ternary silicides as $LaTSi_3$, where T = Rh, Ir [3] and Pd [2] are all superconductors between 1.9 and 2.7 K.

Table 1b

Atomic coordinates and equivalent isotropic displacement parameters for LaPd₂Ge.

Atom site	Wyckoff position	x/a	y/b	z/c	$B_{\rm eq}$. (*10 ² nm ²)	Occupation
La	4 <i>c</i>	0.0310(5)	1/4	0.6536(7)	0.87(9)	1.0
Pd	8 <i>d</i>	0.1768(5)	0.0516(4)	0.0886(6)	1.39(9)	1.0
Ge	4 <i>c</i>	0.3755(9)	1/4	0.3527(13)	0.86(17)	1.0

Table 2b
Atomic coordinates and equivalent isotropic displacement parameters for LaPdGe ₃ .

Atom site	Wyckoff position	x/a	y/b	z/c	$B_{\rm eq} (*10^2 {\rm nm}^2)$	Occupation
La	2a	0	0	0.5999(3)	1.36(4)	1.0
Pd	2a	0	0	0.2496(3)	1.48(6)	1.0
Ge1	4b	0	1/2	0.3587(5)	1.64(4)	1.0
Ge2	2a	0	0	0.0000(5)	1.42(8)	0.93(4)



Fig. 2. The structure of LaPd₂Ge. The truncated polyhedron of the La atoms (a), unit cell and part of the structure as a projection onto XZ- (b) and YZ- (c) planes.



Fig. 3. Temperature dependence of the electrical resistivity of (a) LaPd₂Ge and (b) LaPdGe₃. Upper and lower insets indicate the jumps in the resistivity caused by appearing superconductivity in the former germanide and by the presence of impurities just of the former compound in the latter germanide, while the mid-inset gives a comparison in the resistivity curves $\rho(T)$ of both germanides.

Table 3

Fit's parameters obtained by using Eq. (1) for LaPd₂Ge and LaPdGe₃ compared with the values for La₂PdGe₆ taken from ref. [24].

Compound	$ ho_0 \left(\mu \Omega \mathrm{cm} ight)$	$a (\mu\Omega\mathrm{cm})$	$\Theta_{\mathrm{D}}^{R}(\mathrm{K})$	$K (\mu \Omega \text{ cm } \mathrm{K}^{-3})$
LaPd ₂ Ge:	15.5	144	172	$\begin{array}{c} -1.1\times 10^{-6} \\ 6.9\times 10^{-8} \\ -3.9\times 10^{-7} \end{array}$
LaPdGe ₃	0.53	24	263	
La ₂ PdGe ₆	57	39	195	

Fig. 4 shows two plots of specific heat C_p vs. T measured for LaPd₂Ge and LaPdGe₃ in the temperature range 0.3-16 K in applied magnetic field of zero and 9 T. As seen from this figure, the plots are independent of the magnetic field. In order to see any effect of temperature or field at lowest temperatures in greater detail we show in this figure the respective insets where we plotted the $C_{\rm p}/T$ against T^2 dependence for these two germanides. In the upper inset, there is clearly seen an increase of C_p/T of LaPd₂Ge starting below the temperature agreeing with that of the resistivity data, i.e. about 0.6 K. The limit of 0.37 K of our measurements did not allow to determine a maximum of this anomaly. Hence, it is not possible to give an exact value of $\Delta C / \gamma_n T_c$. A rough estimated value of that is slightly above 0.6, i.e. rather far from the BCS value of 1.43. Typically, a small and broad jump ΔC at T_c is observed when the sample includes impurities or imperfections. A vanishing of the above anomaly under an applied field of 9 T confirms that we deal here with a superconducting behavior of the 1:2:1 germanide. As one can see in the lower inset of Fig. 4, the C_p/T vs. T^2 straight lines derived in zero and 9 T for LaPdGe₃ almost cover each other, despite detecting the low-temperature impurity jump of the resistivity also at around 0.6 K (Fig. 3b). This fact in turn indicates that LaPdGe₃ in opposite to LaPdSi₃ (see Ref. [2]) is not a superconductor down to 0.3 K. The parameters as Sommerfeld coefficient in normal state, γ_n , and Debye temperature, Θ_D , derived from the phonon function: $C_{ph} = \beta T^3$, compared to the known respective values of other phases in the La-Pd-Ge system are displayed in Table 4.

The temperature dependencies of the thermoelectric power, S(T), of both germanides are shown in Fig. 5(a). As seen from this figure, the S(T) functions for these two germanides differ from each other considerably. The Seebeck coefficient for LaPdGe₃ is positive almost in the whole measured temperature range except for the very narrow negative region between 0.8 and 6.8 K, as shown on enlarged S andT scales of Fig. 5(b). As seen further from this figure, this coefficient becomes again positive below 0.8 K. Hence, the low-temperature S(T) function taken for LaPdGe₃ leads to the conclusion that any intrinsic superconducting state of this compound does not exist down to 0.3 K. One may eventually expect a superconducting state but below this temperature, i.e., the temperature limit of our measurements. On the other hand, the low-temperature S(T) function taken for LaPd₂Ge, also displayed in Fig. 5(b), behaves otherwise. At low temperatures, starting at $T_1^* \approx 160$ K this function changes its sign from positive to negative and keeps this sign down to $T_2^* \approx 2$ K, below which it varies as positive thermoelectric power up to its maximum at about 0.8 K. With further decreasing temperature it falls down to create another but small negative maximum just slightly below T_{c} continuing its expected variation to S = 0 at T = 0 K. Moreover, as the upper inset to



Fig. 4. Low-temperature dependence of the C_p vs. *T* function determined at zero and 9 T measured up to 16 K for: (a) LaPd₂Ge and (b) LaPdGe₃. The insets present the corresponding functions C_p/T vs T².The upper inset shows the existence for the former germanide a superconducting transition at $T_c = 0.6$ K at zero- and its lack in an applied magnetic field of 9 T. On the other hand, the same function plotted in the lower inset for the latter germanide illustrates the lack of superconductivity already at zero-field and the measurements taken at 9 T yields an analogues straight-line behavior as that determined at zero-field.

Fig. 5(a) informs such behavior we observe also for a probed superconductor Nb₃Sn [see inset to Fig. 5(a)]. At present we do not know the origin of such a small negative behavior of S(T) just below T_c . Perhaps it is some kind of a relaxation effect. Nevertheless, these both comparable observations may be indicative of that LaPd₂Ge is a real superconductor below 0.6 K. In the insets to Fig. 5(b) we also show the temperature derivatives, dS(T)/dT, taken at temperature region below 1.5 K. In the case of LaPd₂Ge there are apparent two close lying positive maxima in this function, one at T_c being of lower intensity and another one occurring just below T_c being more sharper and with a higher intensity. Oppositely, this quantity for LaPdGe₃ exhibits a broad negative minimum at 0.85 K signalizing an inflection point in the S(T) curve. All these features suggest existing a distinct difference in the Fermi surfaces of



Fig. 5. Thermoelectric power vs. temperature for LaPd₂Ge and LaPdGe₃ taken in ranges: (a) 0.4–300 K and (b) 0.4–5 K. The inset in figure (a) shows the *S* vs. *T* variation for Nb₃Sn around its T_c (17 K), while the lower and upper insets in figure (b) display the temperature derivatives of the thermoelectric power, dS(T)/dT, at temperatures below 1.5 K for both germanides, respectively.

these two compounds. Any further discussion is here difficult by the fact of a lack in the literature of similar data for analogous type of reference compounds to be compared.

Next we will describe the overall temperature behavior of the Seebeck coefficient measured up to 300 K for both germanides. That for LaPdGe₃ goes through a pronounced maximum at $T_{max} \approx 45$ K where S_{max} reaches a value of 3.4 µV/K. Above T_{max} this function decreases rapidly down to 150 K and then saturates to almost a constant value of 1.6 µV/K at RT. A very similar behavior has been reported for LaCu₂Si₂, where *S*(*T*) is also positive at all temperatures and also passes through a maximum at 90 K, and above 250 K saturates to about 2 µV/K [25]. In order to interpret such behavior of *S*(*T*) we will make an application of Mott's relation:

$$S = S_d + S_g \tag{3}$$

where *S* is the sum of both the diffusion, S_d , and phonon-drag, S_g , positive terms. This roughly agrees with the fact that S_g should start

Table 4	4
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Some low-temperature physical parameters of the compounds in La-Pd-Ge ternary system.

Compound	Structure type	<i>T</i> _c (K)	$\gamma(0) (mJ/mol_{La}K^2)$	$\Theta_{\rm D}({\rm K})$	Refs.
LaPd _{0.6} Ge _{1.4}	AlB ₂	2.8	9	300	[2]
LaPd ₂ Ge	YPd ₂ Si	0.6	5.1	213	This work
LaPd ₂ Ge ₂	ThCr ₂ Si ₂	1.10	8.26	291	[9]
$La_3Pd_4Ge_4$	U ₃ Ni ₄ Si ₄	2.50	27.0	256	[9]
La ₂ Pd ₃ Ge ₅	U ₂ Co ₃ Si ₅	_	4.7	326	[2]
La ₂ PdGe ₆	Ce ₂ GaGe ₆	_	3.6	343	[24]
La ₃ Pd ₂₀ Ge ₆	Mg ₃ Ni ₂₀ B ₆	_	33.2	242	[27]
LaPdGe ₃	BaNiSn ₃	-	3.4	295	This work

to decrease in the vicinity $\Theta_D/5$, i.e. in our case after about 30–50 K, which is indeed observed. Thus, these two components and overall magnitudes of the Seebeck coefficient are comparable of many simple metals (e.g. Cu [26]). Therefore this feature and very weak temperature dependence of the resistivity give a base to regard LaPdGe₃ as a typical metal. Finally, the different *S*(*T*) behavior for LaPd₂Ge is easy to explain by assuming that *S*_g has a negative sign, but *S*_d is positive and varies proportionally to temperature along with Mott's formula:

$$S_{\rm d}(T) = x\pi^2 k_{\rm B}^2 T / 3eE_{\rm F} \tag{4}$$

Such a distinct straight-line dependence of S(T) is just seen in Fig. 5a for LaPd₂Ge above about $T^*_1 = 160$ K, i.e. at the temperature where S(T) changes its sign from negative to positive. It is clear that the negative contribution of S_g to the total thermoelectric power of the 1:2:1 germanide shifts the intersection of the extrapolated to T = 0 K straight line with the ordinate axis by about -5μ V/K from the beginning of the coordinate system. The magnitude of the slope of this straight-line derived from this figure yields $E_F \approx 0.74$ eV. It is interesting to underline that the phonon-drag contribution differs in shape in comparison with that found for the 1:1:3 germanide. Instead, having a regular maximum as that found for LaPdGe₃ it becomes more flat with a small overlapped negative maximum at about 20 K.

In summary, we have measured and analyzed the temperature dependences of electrical resistivity, specific heat and thermoelectric power for two ternary germanides: LaPd₂Ge and LaPdGe₃. We have also made the powder refinement of their structures and determined their low-temperature physical properties. We have found that the former germanide is indeed a superconductor below 0.6 K while the latter germanide is a good metal but without transition to the superconducting state at least down to 0.3 K.

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