A new glance on the $R_2M\mathrm{Ge}_6$ (R = rare earth metal, M=another metal) compounds. An experimental and theoretical study of $R_2\mathrm{PdGe}_6$ germanides

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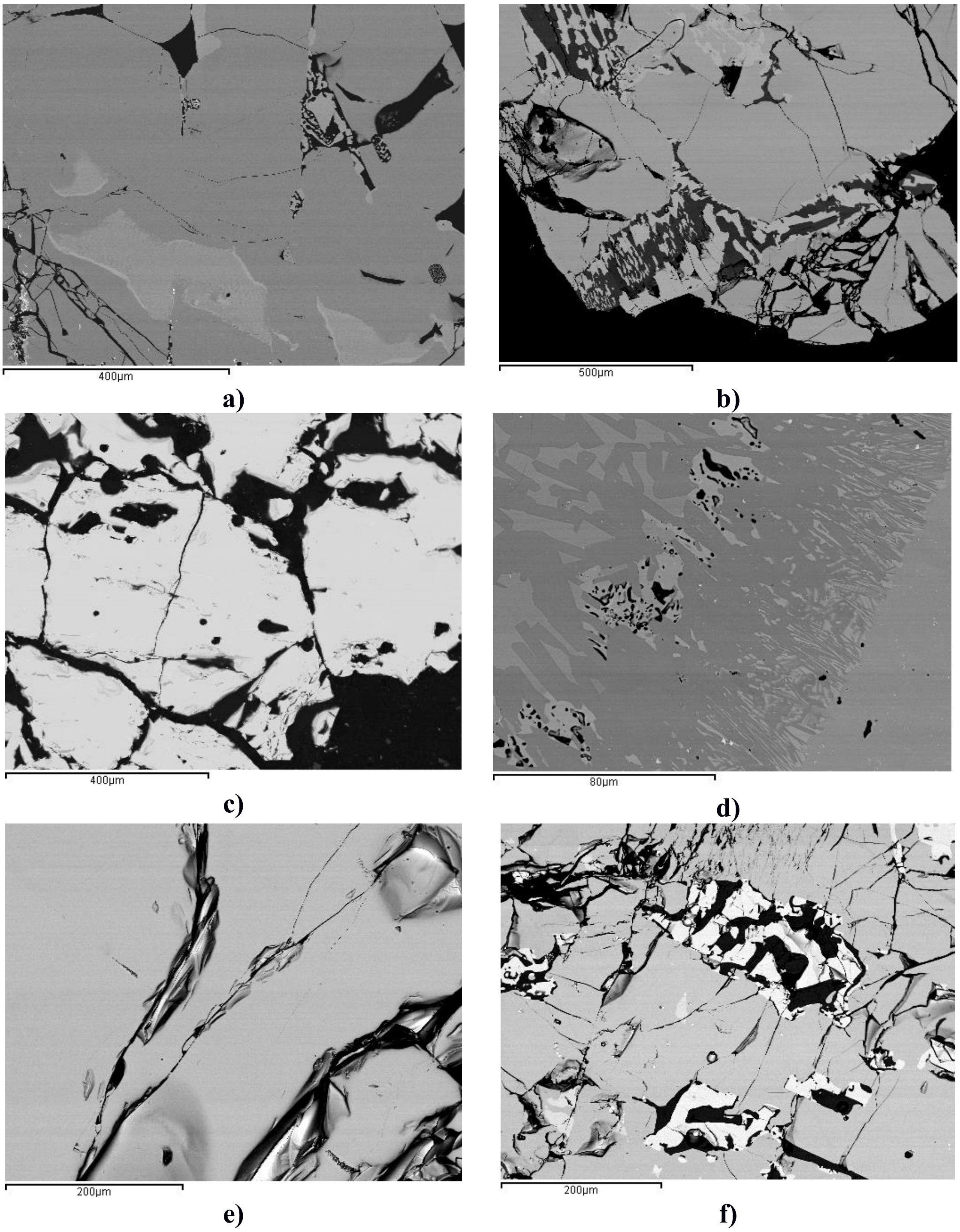

Figure S1. Micrographs of selected $R_{22.1}Pd_{11.1}Ge_{66.7}$ alloys prepared by direct synthesis in resistance furnace:

a) R = Pr: $\mathbf{Pr_2PdGe_6}$ (grey phase); $\mathbf{Pr_2Pd_3Ge_5}$ (light grey phase); **Ge** (dark phase)

b) R = Nd: $\mathbf{Nd_2PdGe_6}$ (grey phase); $\mathbf{Nd_2Pd_3Ge_5}$ (bright phase); **Ge** (dark phase)

c) R = Sm: $\mathbf{Sm_2PdGe_6}$ (bright phase). No other phases are visible in this area.

d) R = Er: $\mathbf{Er_2PdGe_6}$ (dark grey phase); $\mathbf{Er(Pd_xGe_{1-x})_2}$ (light grey phase on the right). Other phases are unknown ternary germanides, still to be investigated.

e) R = Yb: $\mathbf{Yb_2PdGe_6}$ (grey phase). No other phases are visible in this area.

f) R = Lu: $\mathbf{Lu_2PdGe_6}$ (grey phase); $\mathbf{Lu(Pd_xGe_{1-x})_2}$ (bright phase); Ge (dark phase)

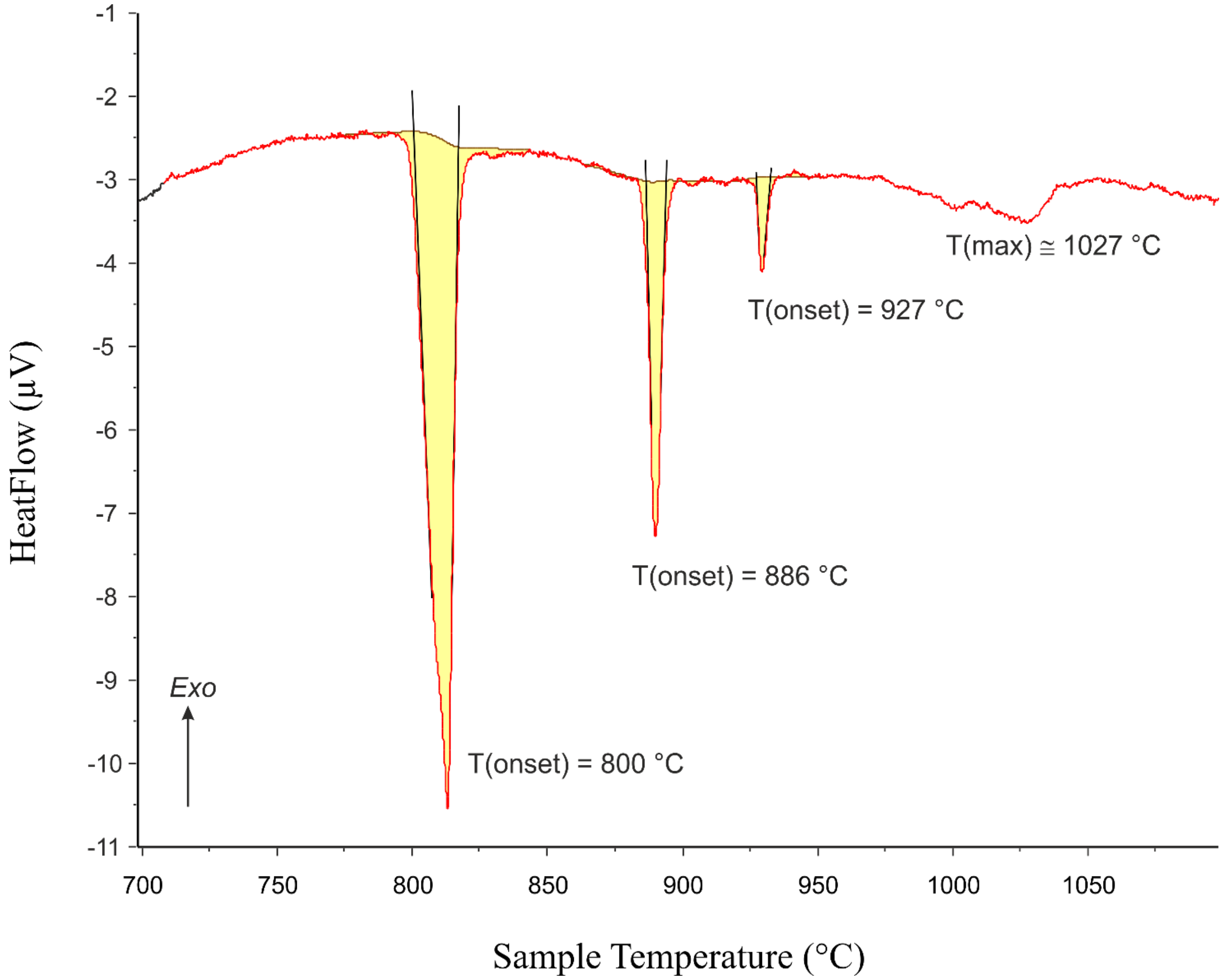

Figure S2. Differential Thermal Analysis curve (heating regime; 5°C/min) for an arc melted sample of nominal composition $La_{21}Pd_7Ge_{72}$.

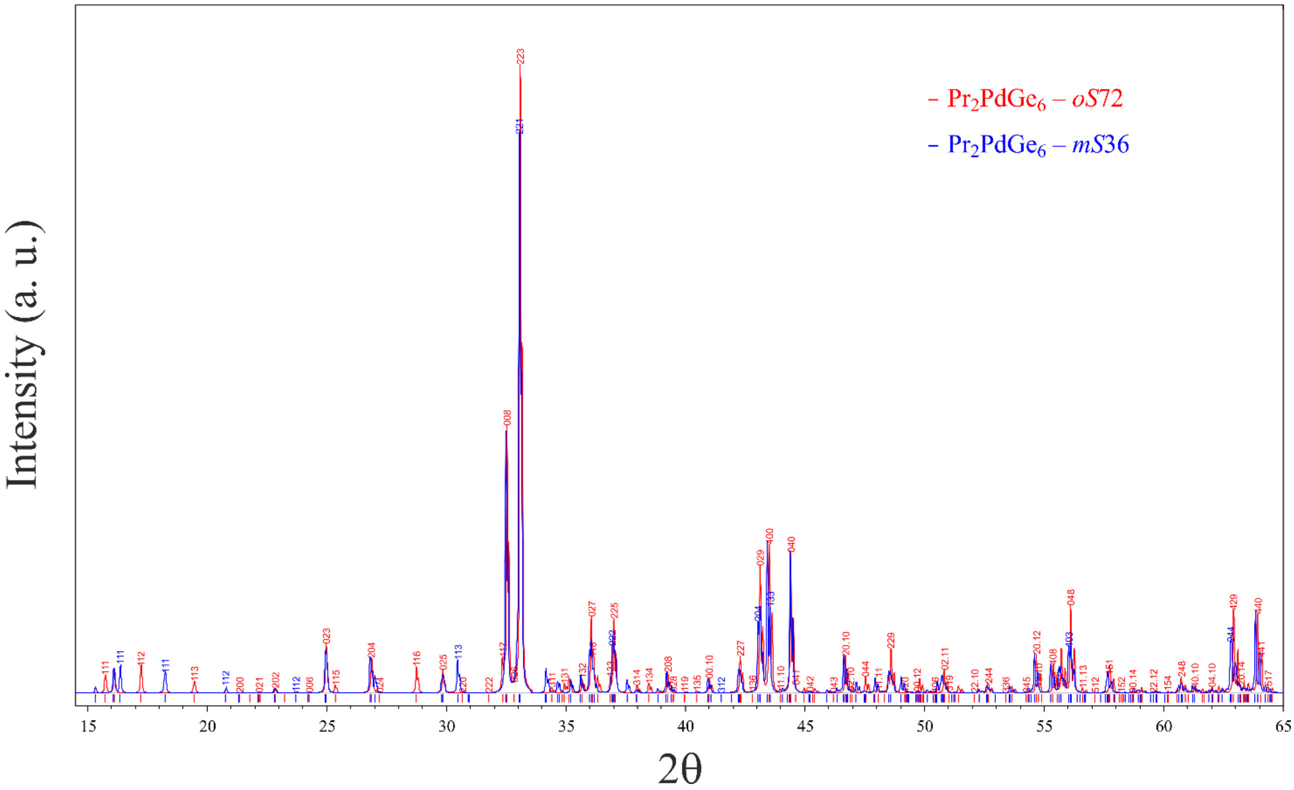

Figure S3. Calculated X-ray powder patterns for Pr_2PdGe_6 with *oS*72 and *mS*36 unit cells (structural data are taken after the structure solution and refinement performed in this work for samples prepared by direct synthesis and by In-flux, respectively).

Table S1. Synthetic conditions applied in order to synthesize and isolate a La_2PdGe_6 single crystal (+ means that the phase of interest has been detected in the sample, - means that it has not been detected).

Nominal composition	**Treatment**	**La_2PdGe_6**	**Comments**
$La_{22.2}Pd_{11.1}Ge_{66.7}$	Induction or arc melting	–	$La(Pd,Ge)_{2-x}$ + $LaPdGe_3$ + Ge
$La_{22.2}Pd_{11.1}Ge_{66.7}$	Induction melting + annealing at 700 °C for 2 w	–	$La(Pd,Ge)_{2-x}$ + $LaPdGe_3$ + Ge
$La_{22.2}Pd_{11.1}Ge_{66.7}$	Cycle I	+	Thin border around $La(Pd,Ge)_{2-x}$
$La_{22.2}Pd_{11.1}Ge_{66.7}$	Cycle I + annealing at 500 °C for 2 w	+	Thin border around $La(Pd,Ge)_{2-x}$
$La_{22.2}Pd_{11.1}Ge_{66.7}$	Cycle I + annealing at 700 °C for 2 w	–	$La(Pd,Ge)_{2-x}$ + $LaPdGe_3$ + Ge
$La_{22.2}Pd_{11.1}Ge_{66.7}$	1-3 DTA cycles (max T = 1100 °C, heating/cooling rate = 5 °C/min) on arc melted sample	+	Border around $La(Pd,Ge)_{2-x}$ and around $LaPdGe_3$ (in some regions border is thick)
$La_{22.2}Pd_{11.1}Ge_{66.7}$	Annealing at 825 °C (30 min) during cooling in DTA of an arc melted sample	–	$La(Pd,Ge)_{2-x}$ + $LaPdGe_3$ + Ge
$La_{22.2}Pd_{11.1}Ge_{66.7}$	Annealing at 880 °C (30 min) during cooling in DTA of an arc melted sample	–	$La(Pd,Ge)_{2-x}$ + $LaPdGe_3$ + Ge
$La_{22.2}Pd_{11.1}Ge_{66.7}$	Arc melting + annealing at 1000 °C for 1 day	–	$La(Pd,Ge)_{2-x}$ + $LaPdGe_3$ + Ge (not clear microstructure)
$La_{22.2}Pd_{11.1}Ge_{66.7}$	Arc melting + annealing at 1000 °C for 1 day + annealing at 890 °C for 1 month	–	$La(Pd,Ge)_{2-x}$ + $LaPdGe_3$ + Ge
$La_{22.2}Pd_{11.1}Ge_{66.7}$	Arc melting + annealing at 1000 °C for 1 day + annealing at 890 °C for 1 month + annealing at 830 °C for 1 month	–	$La(Pd,Ge)_{2-x}$ + $LaPdGe_3$ + Ge
$La_{21}Pd_7Ge_{72}$	Synthesis in In flux cycle II (global composition measured in the region of sample after DTA with big yield of 2:1:6)	+	Crystals of $La(Pd,Ge)_{2-x}$ with border of 2:1:6
$La_{21}Pd_{15}Ge_{64}$	Synthesis in In flux cycle II (global composition chosen to avoid $La(Pd,Ge)_{2-x}$)	+	Small amount around $La(Pd,Ge)_{2-x}$ + In-Pd binary phases crystals
$La_{21}Pd_7Ge_{72}$	Synthesis in In flux cycle II modified (without intermediate annealings)	+	Crystals of $La(Pd,Ge)_{2-x}$ with border of 2:1:6
$La_{21}Pd_7Ge_{72}$	Synthesis in In flux cycle III	+	Many small crystals of “pure” 2:1:6 (no border)

Cycle I 25°C (10°C/min) → 950°C → 350°C (-0.2°C/min) → furnace switched off
Cycle II 25°C → (2°C/min) → 1000°C (5 h) → (-1.0°C/min) → 850°C(48h) → (-0.3°C/min) → 25°C
Cycle III 25°C → (10°C/min) → 750°C (24 h) → (-0.5°C/min) → 25°C

Table S2. Interatomic distances (<3.5 Å) for R_2PdGe_6 (*R*=Y, Ce, Pr, Nd, Er, Yb, Lu) crystallizing with the *oS*72 modification.

Atom 1	Atom 2	*R*=Y *d* [Å]	*R*=Ce *d* [Å]	*R*=Pr *d* [Å]	*R*=Nd *d* [Å]	*R*=Er *d* [Å]	*R*=Yb *d* [Å]	*R*=Lu *d* [Å]
R	Ge3	2.957(1)	3.053(1)	3.054(1)	3.039(1)	2.925(1)	2.970(1)	2.901(1)
	Ge3	3.016(1)	3.092(1)	3.092(1)	3.075(1)	2.993(1)	3.034(1)	2.972(1)
	Ge2	3.057(1)	3.113(1)	3.113(1)	3.100(1)	3.036(1)	3.055(1)	3.023(1)
	Ge2	3.109(1)	3.144(1)	3.144(1)	3.137(1)	3.084(1)	3.105(1)	3.053(1)
	Ge6	3.144(1)	3.203(1)	3.203(1)	3.191(1)	3.121(1)	3.120(1)	3.107(1)
	Ge6	3.150(1)	3.205(1)	3.204(1)	3.194(1)	3.128(1)	3.131(1)	3.118(1)
	Pd	3.151(1)	3.218(1)	3.218(1)	3.206(1)	3.129(1)	3.149(1)	3.108(1)
	Pd	3.156(1)	3.219(1)	3.219(1)	3.207(1)	3.132(1)	3.150(1)	3.115(1)
	Ge5	3.153(1)	3.225(1)	3.225(1)	3.212(1)	3.124(1)	3.169(1)	3.103(1)
	Ge4	3.180(1)	3.232(1)	3.232(1)	3.221(1)	3.156(1)	3.178(1)	3.147(1)
	Ge2	3.124(1)	3.237(1)	3.237(1)	3.218(1)	3.098(1)	3.180(1)	3.095(1)
	Ge3	3.365(1)	3.368(1)	3.368(1)	3.365(1)	3.359(1)	3.351(1)	3.371(1)
Ge2	Ge2	2.448(1)	2.488(1)	2.488(2)	2.483(3)	2.446(1)	2.440(1)	2.439(2)
	Pd	2.448(1)	2.520(1)	2.520(1)	2.505(1)	2.430(1)	2.449(1)	2.418(1)
	Ge3	2.522(1)	2.532(1)	2.532(2)	2.528(3)	2.513(1)	2.490(1)	2.511(2)
	2*R*	3.057(1)	3.113(1)	3.113(1)	3.100(2)	3.036(1)	3.055(1)	3.023(1)
	2*R*	3.109(1)	3.144(1)	3.144(1)	3.137(2)	3.084(1)	3.105(1)	3.053(1)
	2*R*	3.124(1)	3.237(1)	3.237(1)	3.218(1)	3.098(1)	3.180(1)	3.095(1)
Ge3	Ge2	2.522(1)	2.532(1)	5.532(2)	2.528(3)	2.513(1)	2.490(1)	2.511(2)
	Ge3	2.653(1)	2.585(1)	2.585(2)	2.597(3)	2.668(1)	2.583(1)	2.697(2)
	2*R*	2.957(1)	3.053(1)	3.054(1)	3.039(2)	2.925(1)	2.970(1)	2.901(1)
	2*R*	3.016(1)	3.092(1)	3.092(1)	3.075(2)	2.993(1)	3.034(1)	2.972(1)
	2*R*	3.365(1)	3.368(1)	3.368(1)	3.365(1)	3.359(1)	3.351(1)	3.371(1)
Ge4	Ge5	2.503(1)	2.495(1)	2.495(1)	2.496(1)	2.505(1)	2.499(1)	2.506(1)
	Pd	2.493(1)	2.523(1)	2.523(1)	2.518(1)	2.481(1)	2.505(1)	2.476(2)
	2Ge6	2.547(1)	2.581(1)	2.581(1)	2.572(1)	2.533(1)	2.542(1)	2.525(1)
	2*R*	3.180(1)	3.232(1)	3.232(1)	3.221(1)	3.156(1)	3.159(1)	3.147(1)
	2Ge6	3.186(1)	3.241(1)	3.241(1)	3.232(1)	3.167(1)	3.178(1)	3.150(1)
Ge5	Ge4	2.503(1)	2.495(1)	2.495(1)	2.496(1)	2.505(1)	2.498(1)	2.506(1)
	Pd	2.500(1)	2.524(1)	2.524(1)	2.519(1)	2.488(1)	2.505(1)	2.482(1)
	2Ge6	2.547(1)	2.581(1)	2.581(1)	2.574(1)	2.531(1)	2.542(1)	2.524(1)
	2*R*	3.153(1)	3.225(1)	3.225(1)	3.212(1)	3.124(1)	3.159(1)	3.103(1)
	2Ge6	3.287(1)	3.241(1)	3.241(1)	3.230(1)	3.168(1)	3.169(1)	3.150(1)
Ge6	Ge6	2.493(1)	2.487(1)	2.487(1)	2.489(1)	2.496(1)	2.490(1)	2.495(1)
	Pd	2.514(1)	2.549(1)	2.549(1)	2.541(1)	2.499(1)	2.520(1)	2.491(1)
	Ge4	2.547(1)	2.581(1)	2.581(1)	2.572(1)	2.533(1)	2.542(1)	2.525(1)
	Ge5	2.547(1)	2.581(1)	2.581(1)	2.574(1)	2.531(1)	2.542(1)	2.525(1)
	R	3.144(1)	3.203(1)	3.203(1)	3.191(1)	3.121(1)	3.149(1)	3.107(1)
	R	3.150(1)	3.205(1)	3.204(1)	3.194(1)	3.128(1)	3.150(1)	3.118(1)
	Ge5	3.187(1)	3.241(1)	3.241(1)	3.230(1)	3.168(1)	3.159(1)	3.150(1)
	Ge4	3.186(1)	3.241(1)	3.241(1)	3.232(1)	3.167(1)	3.159(1)	3.150(1)
Pd	Ge2	2.448(1)	2.519(1)	2.520(1)	2.505(1)	2.430(1)	2.449(1)	2.418(1)
	Ge4	2.493(1)	2.523(1)	2.523(1)	2.518(1)	2.481(1)	2.498(1)	2.476(1)
	Ge5	2.500(1)	2.524(1)	2.524(1)	2.519(1)	2.488(1)	2.499(1)	2.482(1)
	2Ge6	2.514(1)	2.549(1)	2.549(1)	2.541(1)	2.499(1)	2.520(1)	2.491(1)
	2*R*	3.151(1)	3.218(1)	3.218(1)	3.206(1)	3.129(1)	3.120(1)	3.108(1)
	2*R*	3.156(1)	3.219(1)	3.219(1)	3.207(1)	3.132(1)	3.131(1)	3.115(1)

Table S3. Interatomic distances (<3.5 Å) for R_2PdGe_6 (R=La, Pr) crystallizing with the *mS*36 modification.

Atom 1	Atom 2	*R*=La *d* [Å]	*R*=Pr *d* [Å]
R	Ge3	3.119(1)	3.064(1)
	Ge3	3.126(1)	3.089(1)
	Ge2	3.141(1)	3.112(1)
	Ge2	3.180(1)	3.153(1)
	Ge6	3.232(1)	3.205(1)
	Ge6	3.239(1)	3.206(1)
	Pd	3.259(1)	3.221(1)
	Pd	3.265(1)	3.223(1)
	Ge4	3.264(1)	3.230(1)
	Ge5	3.271(1)	3.237(1)
	Ge2	3.297(1)	3.243(1)
	Ge3	3.382(1)	3.373(1)
Ge2	Ge2	2.520(1)	2.512(1)
	Ge3	2.525(1)	2.511(1)
	Pd	2.570(1)	2.523(1)
	2*R*	3.141(1)	3.112(1)
	2*R*	3.180(1)	3.153(1)
	2*R*	3.297(1)	3.243(1)
Ge3	Ge2	2.525(1)	2.511(1)
	Ge3	2.582(1)	2.612(1)
	2*R*	3.119(1)	3.064(1)
	2*R*	3.126(1)	3.089(1)
	2*R*	3.382(1)	3.373(1)
Ge4	Ge4	2.488(1)	2.503(1)
	Pd	2.542(1)	2.526(1)
	2Ge6	2.598(1)	2.584(1)
	2*R*	3.265(1)	3.230(1)
	2Ge6	3.283(1)	3.245(1)
Ge5	Ge5	2.478(1)	2.494(1)
	Pd	2.542(1)	2.527(1)
	2Ge6	2.598(1)	2.583(1)
	2*R*	3.271(1)	3.237(1)
	2Ge6	3.282(1)	3.246(1)
Ge6	Ge6	2.476(1)	2.493(1)
	Pd	2.575(1)	2.553(1)
	Ge4	2.598(1)	2.584(1)
	Ge5	2.598(1)	2.583(1)
	R	3.232(1)	3.205(1)
	R	3.239(1)	3.206(1)
	Ge5	3.282(1)	3.246(1)
	Ge4	3.283(1)	3.245(1)
Pd	Ge4	2.5420(2)	2.526(1)
	Ge5	2.5424(2)	2.527(1)
	Ge2	2.5697(3)	2.523(1)
	2Ge6	2.5754(2)	2.553(1)
	2*R*	3.2587(2)	3.221(1)
	2*R*	3.2647(2)	3.223(1)