Superconductivity in the New Platinum Germanides $M$Pt$_4$Ge$_{12}$
(M = Rare-earth and Alkaline-earth Metals) with Filled Skutterudite Structure

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New germanium-platinum compounds with the filled-skutterudite crystal structure were synthesized. The structure and composition were investigated by X-ray diffraction and microprobe analysis. Magnetic susceptibility, specific heat, and electrical resistivity measurements evidence superconductivity in LaPt$_4$Ge$_{12}$ and PrPt$_4$Ge$_{12}$ below 8.3 K. The parameters of the normal and superconducting states were established. Strong coupling and a crystal electric field singlet groundstate is found for the Pr compound. Electronic structure calculations show a large density of states at the Fermi level. Similar behavior with lower $T_c$ was observed for SrPt$_4$Ge$_{12}$ and BaPt$_4$Ge$_{12}$.

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Due to the wealth of topical behaviors, compounds with crystal structures composed of rigid covalently bonded cage-forming frameworks enclosing differently bonded guest atoms currently attract much attention. These are in particular the families of skutterudites and clathrates. The increasing interest and efforts to understand the underlying physics and chemistry is motivated by the fascinating diversity of observed physical properties which are due to subtle host-guest interactions and are, moreover, accessible to tuning. For the skutterudites they range from magnetic and quadrupole ordering to heavy-fermion and non-Fermi liquids, fluctuating valency, superconductivity, itinerant ferromagnetism, and even half-metallicity [1, 2, 3]. Also, promising applications as thermoelectric materials considerably boost the popularity of these compounds [1, 2, 3].

The generic class of “skutterudites” derives from the archetype mineral skutterudite CoAs$_3$. The general formula of filled skutterudites is $M_i T_i X_{12}$, where $M$ is an electropositive cation, $T$ – until now – a transition metal of the iron or cobalt group, and $X$ a pnicogen (P, As, or Sb). The cations $M$ reside in icosahedral cages formed by tilted $[TX_6]$ octahedra with inter-octahedral $X$–$X$ bonds. The bonding situation in filled skutterudites can be understood as an electron donation from the guest atoms $M$ to the polyanionic framework [1, 6]. The binary skutterudites of cobalt group elements are diatomic semiconductors with a valence electron count of 72 per $[T_i X_{12}]$ formula unit (assuming a two-center two-electron bonding for $T$–$X$ and $X$–$X$ and a spin-paired $d^6$ configuration for $T^{3+}$) [1]. In the iron-group metal-pnicogen skutterudites the $d^6$-configuration of $T^{3+}$ is not any more sufficient, and cations have to be embedded. The structure motif becomes stabilized for NaFe$_3$Sb$_{12}$ already with 70 electrons per f.u. [6]. The resulting electron deficiency induces metallicity associated with paramagnetism and in some cases collective magnetism [1, 2, 3].

The aforementioned facts suggest a certain flexibility of the crystal structure with respect to the total electron numbers. There are several ways of tuning the electron count and thus the physical properties of skutterudites: i) by the selection of an appropriate guest; ii) by replacing part of the pnicogen atoms by elements of the 14th or 16th group; iii) by substituting the transition-metal atoms, or by combining these approaches. This chemical access to the electronic properties proved already extremely successful in the quest to enhance the thermoelectric properties of skutterudites [1, 3], and moreover provides a high degree of freedom for explorative synthetic work. Thus, from this point of view it seemed particularly interesting if a skutterudite structure could be stabilized composed of other cage-forming elements than pnictogens. The recent resurgence in interest in germanium-based clathrates and the promising electronic applications of these framework structures [2, 8, 9, 11] motivated us to search for chemically compatible compounds which might be accessible to standard semiconductor technologies. Indeed, there exist several skutterudite-related structures with cobalt-group transition-metals where the pnicogen atoms are replaced by one half each of Ge or Sn and group 16 elements thus retaining the electronic balance [11, 12].

In this Letter we report our successful efforts to synthesize the new skutterudite-like compounds $M$Pt$_4$Ge$_{12}$ composed of germanium and, for electronic balance reasons, platinum as a transition metal. They accommodate La and Pr as well as other elements (e.g. $M$ = Sr, Ba, Ce, Nd, Eu) [12, 13] as cations. We examined the basic structural properties through X-ray powder diffraction (XRD) and electron probe microanalysis (EPMA). The physical properties were determined through thermodynamic and transport measurements. We observe the appearance of superconductivity with transition temperatures $T_c$ of 8.3 K for LaPt$_4$Ge$_{12}$ and – unexpectedly high – 7.9 K for PrPt$_4$Ge$_{12}$ containing $4f$ electrons. Our experimental data are supported by results of full-potential band structure calculations using the local density approximation. Though SrPt$_4$Ge$_{12}$ and BaPt$_4$Ge$_{12}$ are also super-
conducting we will only describe in detail the two most prominent superconductors.

### Table I: Crystallographic data of superconducting cubic $M\text{Pt}_4\text{Ge}_{12}$ at room temperature. Structure type: LaFe$_4$P$_{12}$. Space group: $I\bar{m}3$, $Z = 2$. Parameters of the superconducting state were derived from the specific heat data.

| $M$ | $a/\text{Å}$ | $T_c/\text{K}$ | $\gamma_\text{N}/\text{mJ mol}^{-1}\text{K}^{-2}$ | $\Delta c_p/\gamma_\text{N}T_c$ | $2\Delta/k_B T_c$ |
|-----|--------------|----------------|-----------------|-----------------|----------------|
| La  | 8.6235(3)   | 8.27           | 75.8            | 1.49            | 1.94           |
| Pr  | 8.6111(6)   | 7.91           | 87.1            | 1.56            | 2.35           |
| Sr  | 8.6509(5)   | $\approx$ 5.4 | 39.9            | 1.13            | –              |
| Ba  | 8.6838(5)   | $\approx$ 5.0 | 34.0            | 1.17            | –              |

Samples were prepared by standard techniques. Elements in stoichiometric amounts were arc-melted on a water-cooled copper hearth inside a glove box with Ar-atmosphere ($O_2$ and $H_2O < 1$ ppm). A high-frequency furnace was used for melting the educts of the Sr and Ba compounds. The compounds were obtained after annealing at 800°C for 7 d in sealed Ta ampoules. Metallographic and EPMA investigations of polished specimens revealed elemental Ge and traces of PtGe$_2$ ($<1$ vol%) as the only impurity phases in the rather porous samples.

EPMA confirmed the ideal composition (La$_{0.95(10)}$Pt$_{3.9(1)}$Ge$_{12.2(2)}$) of the compound. No indications of a homogeneity range La$_y$Pt$_4$Ge$_{12}$ were found: lattice parameters of samples with $y = 0.9, 1.0, 1.1$ are equal within 3 standard deviations. No defect occupation of the cation position was found by full-profile refinements from powder XRD data (for lattice parameters see Table I).

Magnetization was measured down to 1.8 K in a SQUID magnetometer (MPMS XL-7, Quantum Design) in various external fields. The heat capacity was determined by a relaxation-type method on a PPMS (Quantum Design). In the same measurement system electrical resistivity data ($ac$, $\nu = 13.4$ Hz) were collected with a nominal current density of 0.06 A mm$^{-2}$ in several magnetic fields transverse to the current.

The low-field susceptibility (Fig. 1) displays strong diamagnetic signals due to superconducting transitions with onset at 8.29(2) K (La), 7.92(2) K (Pr), 5.45(8) K (Sr), and 4.98(10) K (Ba). While shielding by supercurrents comprises the whole sample volume (zero-field cooled curves, considering demagnetizing factor and the high porosity of the samples) the field-cooling Meissner effect is less than unity. This incomplete Meissner effect is well known to be due to strong pinning. The inset of Fig. 1 shows the paramagnetic susceptibility of the Pr compound. Normal-state $M/H$ ($\mu_0H > H_{c2}(1.8\text{ K})$) is finite at low temperatures indicating a non-magnetic crystal electric field (CEF) groundstate for the praseodymium ions. At high temperatures the effective magnetic moment is $3.55\mu_B$ (Weiss temperature $\theta_P = -6.7(2)\text{ K}$) confirming the presence of Pr in $4f^2$ configuration, i.e. in the trivalent state. The isostructural compounds NdPt$_4$Ge$_{12}$ and EuPt$_4$Ge$_{12}$ with Nd$^{3+}$ and Eu$^{2+}$ ions, respectively (Kramers ions with magnetic CEF groundstates), are not superconducting above 0.48 K and display magnetic order at 0.67 K and 1.7 K [13], in spite of stronger antiferromagnetic interactions (i.e. for $M = \text{Eu}$, $\theta_P = -18.4$ K for $\mu_0H = 0.01$ T from a low-$T$ Curie-Weiss fit.

The specific heats of the two superconductors with the
highest $T_c$ (the La and Pr compounds) in various magnetic fields are presented in Fig. 2. The normal state specific heat of the La compound is well described by a specific model previously applied to other filled skutterudite compounds $[14, 15, 16, 17]$. The results of these fits suggest that – similar as in [Fe$_5$Sb$_{12}$]-based skutterudites – the La atom’s vibrations are well described by a low-energy Einstein term while the polyanionic host [Pt$_4$Ge$_{12}$] can be treated by the low-temperature Debye approximation $c \propto T^3$. The fit in the range of 3–10 K results in a Debye temperature $\Theta_D = 209$ K for the polyanion (16 atoms), Einstein temperature $\Theta_E = 96$ K for the cation, and the Sommerfeld coefficient $\gamma_N = 76$ mJ mol$^{-1}$ K$^{-2}$. For the Pr compound the values are $\Theta_D = 198$ K and $\gamma_N = 87$ mJ mol$^{-1}$ K$^{-2}$ ($\Theta_E$ cannot be determined unambiguously due to the CEF contribution of Pr). $\Theta_D = 198$ K for Sr and 209 K for BaPt$_4$Ge$_{12}$ are very similar, as it can be expected for the same polyanion.

The jumps in $c_p/T$ at $T_c$ were determined by the usual entropy-conserving construction. The relative changes of $\Delta c_p/\gamma_N T_c$ are 1.49 and 1.56 for La and PrPt$_4$Ge$_{12}$, respectively. While this ratio indicates an electronic specific heat $c_{es}(T)$ for $H = 0$ at $T_c/T = 2$ with the $\alpha$-model $[18]$ we obtain energy gap ratios $2\Delta/k_B T_c$ of 1.94 (La) and 2.35 (Pr) (BCS theory $2\Delta/k_B T_c = 1.764$), confirming the strong coupling in the Pr compound.

![Graph](image_url)

**FIG. 3:** (color online) Electrical resistivity of LaPt$_4$Ge$_{12}$ (La) and PrPt$_4$Ge$_{12}$ (Pr) in magnetic fields in steps $\Delta \mu_0 H$ of 0.1 T.

The field dependence of the upper critical field $H_{c2}$ was determined from the midpoints of the jumps in $c_p(T, H)$. The results are given in the inset of Fig. 3 and suggest that $\mu_0 H_{c2}$ varies almost linearly with $T$. In order to confirm this finding the electrical resistivity was measured in several magnetic fields. Results are depicted in Fig. 4 for equally spaced field intervals of $\Delta \mu_0 H = 0.1$ T. It is obvious from the zero-resistance points of the curves $(\rho(T, H) = 0)$ that $T_c(H)$ varies linearly with the applied field. An extrapolation (see Fig. 2 inset) yields $\mu_0 H_{c2}(0) = 1.60$ T and 2.06 T for La and PrPt$_4$Ge$_{12}$, respectively.

The residual and room temperature resistivities of the current porous polycrystalline samples are surprisingly low: 5.3 and 177 $\mu\Omega$ cm for $M = $ La and 2.6 and 110 $\mu\Omega$ cm for $M = $ Pr. Therefore the superconductivity is assumed to be in the clean limit. The magnetoresistance ratio $(\rho(H) - \rho(0))/\rho(0)$ increases strongly with decreasing $T$. For the La compound it amounts to +66% at $\mu_0 H = 9$ T (+23% at 4 T; +9% at 2 T) just above $T_c$. PrPt$_4$Ge$_{12}$ displays similar values (+83% in 9 T).

The presence of superconductivity in a compound containing paramagnetic rare-earth ions is usually destroyed by pair breaking. The CEF leading to a non-magnetic singlet groundstate in PrPt$_4$Ge$_{12}$ can be estimated by calculating the excess specific heat $c_{CEF}(T)$ with respect to the La compound. The resulting heat capacity can be fitted with a Schottky anomaly with an energy level scheme for the $^3H_4$ ground multiplet of the $4f^2$ state of Pr$^{3+}$ on a site with cubic point symmetry $T_h (m3)$ $[19]$. We find a $\Gamma_3$ singlet as groundstate, the non-magnetic doublet $\Gamma_2$ at a splitting of $\Delta E/k_B = 93(5)$ K and the two triplets $\Gamma_4$ at 159(10) K and 170(20) K, respectively. The well-isolated non-magnetic CEF groundstate of the Pr obviously leaves the superconductivity in PrPt$_4$Ge$_{12}$ almost undisturbed. For the isostructural compound PrRu$_4$Sb$_{12}$ with a CEF splitting $\Delta E/k_B = 125$ K the $T_c$ is well below that of the corresponding La compound ($T_c = 1.04$ K vs. 3.58 K) $[20]$. Other La and Pr-filled superconducting skutterudite phases based on iron group metals with pnicogen atoms were also reported. While for La$_x$Rh$_4$P$_{12}$ $T_c$ up to 17 K is found the corresponding Pr compound has only a $T_c$ of 2.4 K $[21]$. Thus, PrPt$_4$Ge$_{12}$ is a “van-Vleck superconductor” with a remarkably high $T_c$. In this respect, the reasons for the low magnetic ordering temperatures in the Nd and Eu compounds merit further investigation.

To study the electronic structure of La(Pr)Pt$_4$Ge$_{12}$ a full-potential non-orthogonal local-orbital calculation scheme $[22]$ within the local density approximation was applied. In the full-relativistic calculations, the exchange and correlation potential of Perdew and Wang $[23]$ was used. As the basis set, La(5$s$, 5$p$, 6$s$, 6$p$, 5$d$, 4$f$), Pr (5$s$, 5$p$, 6$s$, 6$p$, 5$d$), Pt(5$s$, 5$p$, 6$s$, 6$p$, 5$d$), and Ge (3$d$, 4$s$, 4$p$, 4$d$) states were employed. All lower-lying states were treated as core states $[24]$. A very dense $k$-mesh of 3333 points in the irreducible part of the Brillouin zone (74088 in the full zone) was used to ensure accurate density of states information, especially in the region close to the Fermi level. An optimization of the cubic crystal struc-
FIG. 4: (color online) Total (upper panel) and atom resolved electronic density of states for \(\text{LaPt}_4\) \(\text{Ge}_{12}\) and \(\text{PrPt}_4\) \(\text{Ge}_{12}\). The inset in the upper panel shows the well-pronounced peak in \(\text{LaPt}_4\) \(\text{Ge}_{12}\) in a narrow region around the Fermi level.

ture \((a, y(\text{Ge}), z(\text{Ge}))\) for the La compound resulted in very good agreement with the powder refinement emphasizing the structural stability of this system.

The calculated total density of states (DOS) for \(\text{LaPt}_4\) \(\text{Ge}_{12}\) in comparison to \(\text{PrPt}_4\) \(\text{Ge}_{12}\) is plotted in Fig. 4 (upper panel). On first glance, the electronic DOS of both compounds is very similar. The contribution of La and Pr to the valence band are very small and featureless. The low-lying bands between about −12 eV and −6 eV are predominantly bonding Ge 6s states. The majority of Pt 5d states is located between about −5.5 eV and −2.5 eV and hybridizes strongly with the Ge 4p orbitals. These facts strongly support the picture of a charge transfer from the rare-earth cation to the \(\text{Pt}_4\) \(\text{Ge}_{12}\) polyanion. The states at the Fermi level \(\varepsilon_F\) are mainly (about 80%) due to Ge 4p bands. At \(\varepsilon_F\) the DOS values are \(\gamma_N = 13.4\) and 9.3 states eV\(^{-1}\) f.u.\(^{-1}\) for the La and the Pr compound, respectively, corresponding to coupling constants \(\lambda = \gamma_N/\gamma_0 = 1.4\) and 2.9. This gives further evidence for the considerably stronger coupling in the \(\text{PrPt}_4\) \(\text{Ge}_{12}\).

In conclusion, we have found new intermetallic compounds of platinum and germanium with the filled-skutterudite crystal structure. The La, Sr, Ba and – most noteworthy – the Pr-filled compounds are superconductors with maximum \(T_c\) around 8 K. Thermodynamic measurements indicate strong coupling for \(\text{PrPt}_4\) \(\text{Ge}_{12}\) and a non-standard variation of \(H_c^2\) with temperature.

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