

## Chemistry and Physics of Filled Skutterudites

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Filled skutterudite compounds exhibit a wealth of topical phenomena. Binary skutterudites  $TX_3$  (structure type  $CoAs_3$ ) are formed by  $T = Co, Rh, Ir$  with pnictogens ( $X = P, As, Sb$ ). In order to stabilize the skutterudite structure with elements of the iron group or other metals it is necessary to “fill” the structure with electropositive elements which leads to a formula  $M_yT_4X_{12}$  (structure type  $LaFe_4P_{12}$ ) [1]. The stabilizing atoms reside in large voids in the transition-metal pnictogen framework (Fig. 1).  $M$  can be an alkali, alkaline-earth, rare-earth or actinide metal or even thallium. Different degrees of filling up to  $y = 1$  can be realized depending on the “filler”  $M$  and the “host”  $[T_4X_{12}]$ . A variety of properties has been observed for rare-earth filled skutterudites (see [2]). Furthermore, interest in these compounds is still heavily fueled by their potential use in thermoelectric devices.

### Skutterudites $MFe_4Sb_{12}$

In the last years we continued to investigate skutterudites with  $[Fe_4Sb_{12}]$  host framework and various non-magnetic fillers. A comprehensive study of the structural, thermal, electronic and transport properties of these filled skutterudites was com-

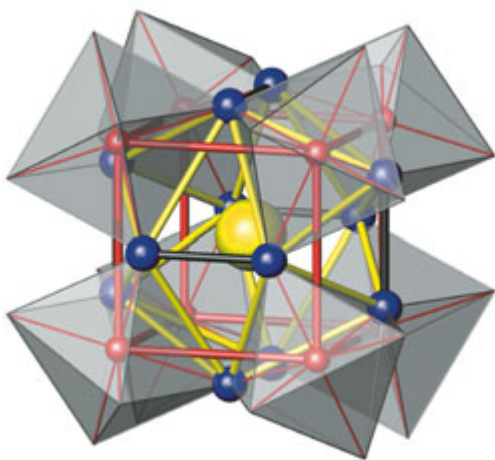


Fig. 1: Section of the crystal structure of filled skutterudites with the general formula  $MT_4X_{12}$ . The  $TX_6$  octahedral units are shown in gray, the icosahedral void is outlined in yellow.

pleted [3,4]. The skutterudites  $NaFe_4Sb_{12}$ ,  $KFe_4Sb_{12}$  and the recently discovered isostructural  $TlFe_4Sb_{12}$  exhibit ferromagnetic order below  $T_C \approx 80$  K with weak itinerant magnetic moments and strong spin fluctuations (SF) [3,5-7]. These compounds are nearly half-metallic ferromagnets (with potential spintronics applications). A large spin polarization was predicted from band structure calculations [3] and could actually be confirmed by point contact spectroscopy indicating a charge carrier spin polarization up to 67 % [8].

The compounds with divalent cations ( $M = Ca, Sr, Ba, Yb$ ) remain paramagnetic down to 2 K. Our electronic structure calculations indicate that the ground state should also be ferromagnetic within the local density approximation. The compounds exhibit huge Sommerfeld-Wilson ratios and are close to ferromagnetism [3,7,9]. However, it is possible to quench the spin fluctuations and to drive these materials towards ordering. One way is the incorporation of strong local magnetic fillers like  $Eu^{2+}$  with  $S = 7/2$  which leads to a ferrimagnetic arrangement of the Eu and Fe spins with  $T_C \approx 86$  K. The induced fields  $B_{ind}$  as observed by Mößbauer spectroscopy in  $NaFe_4Sb_{12}$  (1.64 T) [3] and in  $TlFe_4Sb_{12}$  (0.7 T and 1.8 T) [6] are small. For  $Eu_{0.88}Fe_4Sb_{12}$  similarly small  $B_{ind}$  values (with opposite sign) were observed indicating that the Fe magnetism in the Eu compound and in  $M^{1+}Fe_4Sb_{12}$  is based on the same physics.

Interestingly, these nearly ferromagnetic compounds exhibit a pseudogap in the infrared optical conductivity which appears for  $T < 100$  K [10]. This common phenomenon could be traced back to certain features in the band structure just above the Fermi level  $E_F$ , thus the occurrence of such a pseudogap does not require the presence of strong electronic correlations. The closure of this pseudogap leads to the characteristic hump in the temperature dependence of the electrical resistivity of  $MFe_4Sb_{12}$  ( $M = Ca, Sr, Ba, Yb$ ) at  $\approx 80$  K and interesting, non-standard temperature behavior of other transport properties below 50 K [4].

Skutterudites with trivalent ions are prone to have defects on the filler position which we inves-

tigated in a study on  $\text{La}_y\text{Fe}_4\text{Sb}_{12}$  single crystals. Thus, along with the above set of cations an electron donation to the  $[\text{Fe}_4\text{Sb}_{12}]$  host ranging from 1 to  $\leq 3$  could be realized. This charge transfer leads to a systematic change of the electronic states as already reported [2,4]. On the other hand, the widely varying masses and radii of these cations imply a strong modification of the phonon spectrum of the crystal [4]. In cooperation with *M. Koza et al.* (ILL, France) we have conducted an extensive experimental and theoretical study of the phonon density of states (DOS) of these skutterudites [11]. For the majority of the  $M\text{Fe}_4\text{Sb}_{12}$  skutterudites the vibrations of the cation severely hybridize with those of the host structure. Only for certain heavy cations (La, Nd, Yb) a clear peak in the partial phonon DOS of the cation exists at low energies. The latter could be identified as the supposed decoupled vibrations (“rattling”) of the cation [11]. These findings demonstrate that the phonon glass electron crystal concept (coined by *G.A. Slack* for the development of materials with high thermoelectric performance) is not applicable to real skutterudite materials. This conclusion is corroborated by our observations of the spectral weight contained in the Einstein mode in the specific heat of skutterudites with heavier cations ( $M = \text{Yb}, \text{Tl}$ ) [4,6].

Another investigation addressed the field dependence of the specific heat of  $\text{La}_y\text{Fe}_4\text{Sb}_{12}$ . With more than two transferred electrons the tendency towards ferromagnetic ordering ceases. While the electronic DOS at  $E_F$  decreases in the sequence of the ions  $\text{K}^{1+}$ ,  $\text{Ca}^{2+}$ ,  $\text{La}^{3+}$ , the signature of strong correlations is only visible for the La compound. The field dependence of the specific heat of skutterudites with mono- and divalent cations is weak due to the high energy of the spin fluctuations, which is roughly given by the Weiss temperature  $\theta_p$  ( $\approx 80$  K for  $M = \text{Na}, \text{K}, \text{Tl}$ ,  $\approx 40$  K for  $M = \text{Ca}, \text{Yb}$ ). In contrast, for the La compound, the electronic term  $\gamma(H=0)$  is almost twice as high as that of the other compounds (Fig. 2). This enhancement stems from a contribution  $c_{\text{SF}} = \sigma T^3 \ln(T/T_{\text{SF}})$  due to spin fluctuations. From a fit of a data set taken in several fields the Debye temperature  $\Theta_D = 264$  K (298 K) and a spin fluctuation temperature  $T_{\text{SF}} = 13$  K (17 K) is found for a La filling  $y$  of 0.79 (0.92). The dominant character (ferro- or antiferromagnetic) of the spin fluctuations is, however, not yet fully clarified. The large  $\Theta_D$  for the

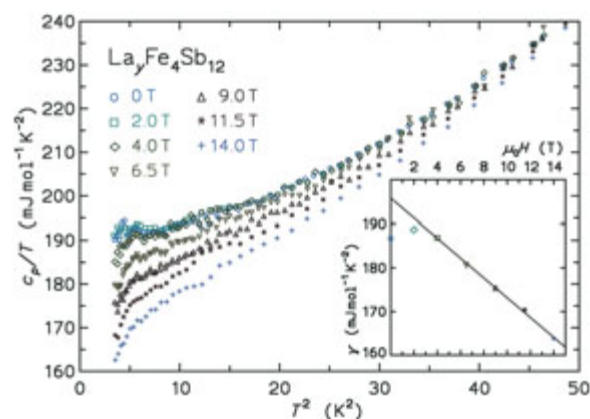


Fig. 2: Magnetic field dependence of the specific heat ( $c_p/T$  vs.  $T^2$  representation) of  $\text{La}_y\text{Fe}_4\text{Sb}_{12}$  ( $y = 0.92$ ) below 7 K. The inset shows  $\gamma(H)$  (symbols) and a linear fit (line).

$\text{La}_y\text{Fe}_4\text{Sb}_{12}$  crystal demonstrates that the chemical bond strength in the polyanion increases with increasing charge transfer.

### **$\text{TlFe}_4\text{Sb}_{12}$ : a Ferromagnetic Skutterudite**

The fact that thallium can be stabilized with an oxidation state of +1, in which it behaves similarly to alkali metals, prompted us to synthesize  $\text{TlFe}_4\text{Sb}_{12}$  [6]. In contrast to Co-skutterudites, in this new compound nearly all icosahedral voids are filled with thallium.  $\text{Tl}^+$  has by far the largest mass of monovalent cations which have been “inserted” in the  $[\text{Fe}_4\text{Sb}_{12}]$  polyanion.  $\text{TlFe}_4\text{Sb}_{12}$  has a crystal structure of  $\text{LaFe}_4\text{P}_{12}$  type [1] with a cubic lattice parameter  $a = 9.1973(5)$  Å, and is—like its Na and K homologues—a ferromagnet with  $T_C = 80$  K. From the chemical analysis a composition of  $\text{Tl}_{0.98(2)}\text{Fe}_{3.97(2)}\text{Sb}_{12.04(2)}$  was deduced, in agreement with the structure refinement resulting in a thallium occupation of 96.1(8)% on the  $2a$  site.

The paramagnetic effective moment is  $3.4 \mu_B/\text{f.u.}$ , i.e., very similar to that of the Na and K homologues. Thus, this value of  $\mu_{\text{eff}}$  represents the magnetism of the  $[\text{Fe}_4\text{Sb}_{12}]$  polyanion.

From the calculated total electronic DOS for  $\text{TlFe}_4\text{Sb}_{12}$  we find that the Tl skutterudite is electronically very close to the alkali-metal compounds. The valence region above  $-5$  eV, which is predominantly formed by Fe  $3d$  and Sb  $5p$  states, shows almost identical width and shape. Thus, Tl in  $\text{TlFe}_4\text{Sb}_{12}$  behaves like a monovalent cation. From the calculated Fermi surface sheets and the band-resolved DOS a strong compensation of hole

and electron charge carriers in the  $\text{TlFe}_4\text{Sb}_{12}$  system is found, in agreement with the measured Hall effect data. From a spin-polarized calculation we find a total magnetic moment of  $2.9 \mu_{\text{B}}/\text{f.u.}$  The calculated ground state is nearly half metallic, the (static) spin polarization is 96%.

The narrow width of the band around  $-6 \text{ eV}$  indicates a rather localized nature of the Tl states, in the language of chemical bonding, that they can be considered as inert pair. The low-lying Tl  $6s$  states only weakly hybridize with the  $5s$  states of the surrounding Sb atoms, albeit significantly stronger than the alkali-metal ions in  $\text{Na/KFe}_4\text{Sb}_{12}$ . Thus, the Tl and the alkali-metal compounds behave electronically similarly, however, the resulting lattice vibrations (especially those of the cations) are very different. In agreement with the calculations it is experimentally found that the Sommerfeld coefficient  $\gamma$  of  $\text{TlFe}_4\text{Sb}_{12}$  is of the size observed for other  $M\text{Fe}_4\text{Sb}_{12}$  with  $M = \text{Na, K, Ca, Sr, Ba, Yb}$  ( $100\text{-}120 \text{ mJ mol}^{-1} \text{ K}^{-2}$ ).

### Superconductivity in Platinum Germanides

The bonding situation in filled skutterudites can be understood as an electron donation from the guest atoms  $M$  to the polyanionic framework [3,12]. Binary skutterudites of cobalt group elements are diamagnetic semiconductors with a valence electron count of 72 per  $[\text{T}_4\text{X}_{12}]$  formula unit. In iron-group metal-pnicogen skutterudites the  $d^5$ -configuration of  $T^{3+}$  is no longer stable, and cations have to be embedded. In the case of  $\text{NaFe}_4\text{Sb}_{12}$  the structure motif becomes stabilized already with 70 valence electrons per f.u. [3]. The resulting electron deficiency induces metallicity associated with paramagnetism and—in some cases—collective magnetism [3,5,12].

These facts suggest a flexibility of the crystal structure with respect to the valence electron numbers. There are several ways of tuning the electron count and thus, the physical properties of skutterudites: i) by selection of an appropriate guest; ii) by replacing the pnicogen atoms by elements of the 14<sup>th</sup> or 16<sup>th</sup> group, iii) by substituting the transition metal. The large interest in germanium-based clathrates and the promising applications of these structures motivated us to search for chemically compatible compounds.

$M$	$a$ [Å]	$T_c$ [K]	$\gamma_N$ [J/(mol K <sup>2</sup> )]	$\Delta c_p/\gamma_N T_c$
La	8.6235(3)	8.27	0.0758	1.49
Pr	8.6111(6)	7.91	0.0871	1.56
Sr	8.6509(5)	$\approx 5.4$	0.0399	1.13
Ba	8.6838(5)	$\approx 5.0$	0.0340	1.17

Table 1:  $M\text{Pt}_4\text{Ge}_{12}$  compounds: space group  $\bar{I}m\bar{3}$ ; lattice parameter  $a$  at 295 K.  $T_c$ , normal-state Sommerfeld coefficient, and normalized jump at  $T_c$  from specific heat data.

We were able to synthesize new skutterudite compounds  $M\text{Pt}_4\text{Ge}_{12}$  composed of germanium and platinum. They accommodate the early rare-earth ions La, Ce, Pr, Nd, Sm,  $\text{Eu}^{2+}$  as well as the alkaline-earth ions Sr and Ba [13].

Samples were prepared by arc or induction melting of the elements under Ar atmosphere and annealing at  $800 \text{ }^\circ\text{C}$  for 7 days in Ta ampoules. EPMA confirmed the composition ( $\text{La}_{0.95(10)}\text{Pt}_{3.9(1)}\text{Ge}_{12.2(2)}$ ). No indication of a homogeneity range  $\text{La}_y\text{Pt}_4\text{Ge}_{12}$  was 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 detected by full-profile refinements of powder XRD data. The cubic lattice parameters (Table 1) are significantly smaller than for  $M\text{Fe}_4\text{Pn}_{12}$  ( $\text{Pn} = \text{P, As, Sb}$ ) skutterudites.

The low-field susceptibility (Fig. 3) displays strong diamagnetic signals due to superconducting transitions with onset at  $8.29(3) \text{ K}$  (La),  $7.92(3) \text{ K}$  (Pr),  $5.4 \text{ K}$  (Sr), and  $5.0 \text{ K}$  (Ba). While shielding by supercurrents comprises the whole sample vol-

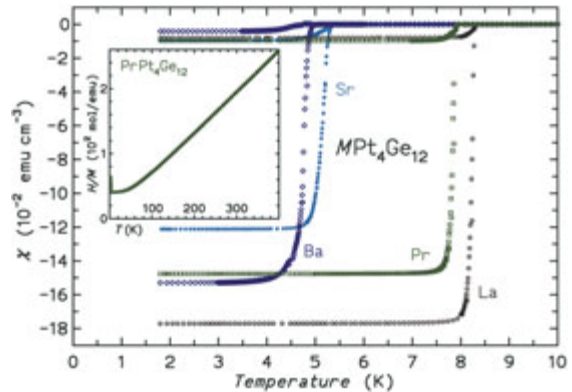


Fig. 3: Magnetic susceptibility  $\chi(T)$  of filled skutterudites  $M\text{Pt}_4\text{Ge}_{12}$  ( $M = \text{Sr, Ba, La, Pr}$ ) for  $\mu_0 H = 2 \text{ mT}$  (nominally). The inset shows the inverse molar susceptibility  $H/M$  of the Pr compound for  $\mu_0 H = 1 \text{ T}$ .

ume (zero-field cooled curves) the field-cooling Meißner effect is one order of magnitude smaller than full flux expulsion. Such a small Meißner effect is well known to result from strong pinning. The normal-state susceptibilities of the Sr, Ba, and La compounds are diamagnetic. The inset of Fig. 3 shows the paramagnetic susceptibility of  $\text{PrPt}_4\text{Ge}_{12}$ . The normal-state susceptibility  $M/H$  saturates below 30 K indicating a non-magnetic crystal electric field (CEF) ground state of the Pr ions. At high temperatures the effective magnetic moment is  $3.67 \mu_B$  (Weiss temperature  $\Theta_p = -16.4(2)$  K) confirming the presence of  $\text{Pr}^{3+}$  ( $4f^2$  configuration) with the  $^3\text{H}_4$  CEF ground multiplet.

The isostructural compounds  $\text{NdPt}_4\text{Ge}_{12}$  ( $a = 8.6074(3)$  Å,  $\text{Nd}^{3+}$ ) and  $\text{EuPt}_4\text{Ge}_{12}$  ( $a = 8.6363(4)$  Å,  $\text{Eu}^{2+}$ ) with magnetic CEF ground states are not superconducting down to 0.48 K and display antiferromagnetic order at only 0.67 K and 1.7 K, respectively, in spite of strong antiferromagnetic interactions (for  $M = \text{Eu}$ ,  $\Theta_p = -18.4$  K for  $\mu_0 H = 0.01$  T from a low-temperature Curie-Weiss fit).

The specific heats of the two compounds with the highest  $T_c$  were investigated in detail [13]. The normal-state specific heat of  $\text{LaPt}_4\text{Ge}_{12}$  is well described by the model already applied to the  $M[\text{Fe}_4\text{Sb}_{12}]$  skutterudite compounds [4,7]. The results of this fit suggest that the La atomic vibrations can be described by a low-energy Einstein term while the host  $[\text{Pt}_4\text{Ge}_{12}]$  is treated by the Debye  $T^3$  approximation. The fit results in a Debye temperature  $\Theta_D = 209$  K for the polyanion, Einstein temperature  $\Theta_E = 96$  K for the cation, and the Sommerfeld coefficient  $\gamma_N = 76$   $\text{mJ mol}^{-1} \text{K}^{-2}$ . For  $\text{PrPt}_4\text{Ge}_{12}$  the values are  $\Theta_D = 198$  K and  $\gamma_N = 87$   $\text{mJ mol}^{-1} \text{K}^{-2}$  ( $\Theta_E$  cannot be determined due to the CEF contribution).  $\Theta_D = 198$  K for Sr and 209 K for  $\text{BaPt}_4\text{Ge}_{12}$  are similar (see also Table 1).

The jumps in  $c_p/T$  at  $T_c$  are  $\Delta c_p/\gamma_N T_c = 1.49$  for  $\text{LaPt}_4\text{Ge}_{12}$  and 1.56 for  $\text{PrPt}_4\text{Ge}_{12}$ . While this ratio indicates a coupling slightly stronger than in the weak coupling BCS limit ( $\Delta c_p/\gamma_N T_c = 1.43$ ) for  $\text{LaPt}_4\text{Ge}_{12}$ , the Pr compound is a strong-coupling superconductor. From the electronic specific heat we obtain energy gap ratios  $\Delta/k_B T_c$  of 1.94 (La) and 2.35 (Pr) [13]. Our recent heat capacity measurements down to 0.4 K [14] confirm the conclusions of the original publication [13] and revealed a clear  $T^3$  dependence of the electronic specific heat  $c_e$  in the superconducting state for  $T/T_c < 0.2$  in both superconductors (Fig. 4). This surprising

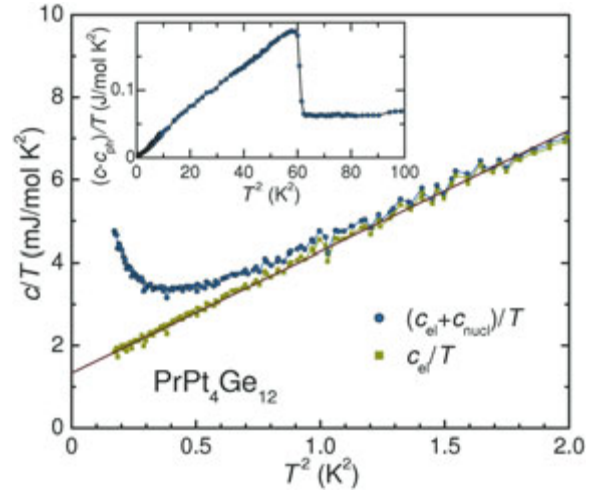


Fig. 4: Inset: specific heat capacity  $c - c_{ph}/T$  of  $\text{PrPt}_4\text{Ge}_{12}$  corrected for the phonon contribution. The main panel shows the electronic specific heat  $c_{el}$  and the nuclear contribution  $c_{nucl}$ .

observation provides evidence for the gap function of both  $\text{LaPt}_4\text{Ge}_{12}$  and  $\text{PrPt}_4\text{Ge}_{12}$  having point nodes [14]. Therefore, a study using transverse-field muon spin rotation ( $\mu\text{SR}$ ) as a probe for the temperature dependence of the superfluid density was commenced in cooperation with scientists from the Laboratory for Muon Spin Spectroscopy at the PSI, Switzerland. A confirmation of the nodal gap structure as suggested by the specific heat results was obtained and the symmetry of the gap function could be narrowed down to two possible models with point nodes [14].

The temperature dependence of the upper critical field  $H_{c2}$  was determined from the midpoints of the jumps in  $c_p(T, H)$  down to 2.5 K [13]. Electrical resistivity data down to 0.4 K confirmed the data. Taking the zero-resistance points of the curves yields  $T_c(H)$  data which vary unconventionally linear with  $H$ . An extrapolation yields  $\mu_0 H_{c2}(0) = 1.60$  T ( $\text{LaPt}_4\text{Ge}_{12}$ ) and 1.82 T ( $\text{PrPt}_4\text{Ge}_{12}$ ). The residual resistivities  $\rho_0$  of our polycrystalline samples are quite low ( $\rho_{300\text{K}}/\rho_0 \geq 33$  for  $M = \text{La}$  and 42 for  $M = \text{Pr}$ ) indicating good sample quality. Thus, the superconductivity is in the clean limit as also confirmed by the  $\mu\text{SR}$  results [14].

The presence of superconductivity in a compound containing paramagnetic rare-earth ions is usually destroyed by pair breaking. The CEF scheme leading to a non-magnetic ground state in  $\text{PrPt}_4\text{Ge}_{12}$  can be estimated in two ways. Firstly, by calculating the excess specific heat  $c_{\text{CEF}}(T)$  with respect to the La compound:  $c_{\text{CEF}}$  can be fitted

with a Schottky anomaly using an energy level scheme for the  $^3H_4$  multiplet on a site with cubic point symmetry  $T_h (m\bar{3})$  [15]. Secondly, the paramagnetic susceptibility can be approximated with a special CEF model. Due to the small  $4f$  contribution to  $c_p(T)$  the latter method results in a more reliable level scheme. Invariably, we find the  $\Gamma_1$  singlet as ground state and the  $\Gamma_{4(1)}$  triplet at  $\Delta E/k_B = 131(2)$  K. The higher levels depend sensitively on the CEF parameters. The best fit of the  $4f$  contribution of  $\chi(T)$  results in the non-magnetic doublet  $\Gamma_{23}$  at 226 K and the triplet  $\Gamma_{4(2)}$  at 295 K. The well-isolated non-magnetic CEF ground state of the Pr obviously leaves the superconductivity in  $\text{PrPt}_4\text{Ge}_{12}$  almost undisturbed. This is not the case in the pnictide-based skutterudites which have significantly larger lattice parameters. For  $\text{PrRu}_4\text{Sb}_{12}$  with a  $\Gamma_{4(1)}$  first excited state at  $\Delta E/k_B = 73$  K the  $T_c$  is well below that of the corresponding La compound ( $T_c = 1.04$  K vs. 3.58 K). Other La/Pr-filled skutterudites are  $\text{La/PrRu}_4\text{As}_{12}$  with  $T_c$  of 10.3 K and 2.33 K, respectively [15]. For  $\text{La}_3\text{Rh}_4\text{P}_{12}$  a  $T_c$  of up to 17 K is found while the Pr compound has only a  $T_c$  of 2.4 K. The remarkably high  $T_c$  of  $\text{PrPt}_4\text{Ge}_{12}$  and the low magnetic ordering temperatures of the Nd and Eu compounds are subject of further investigations, e.g., by NMR spectroscopy [16].

To study the electronic structure of  $\text{La(Pr)Pt}_4\text{Ge}_{12}$  the FPLO package within the local density approximation was applied. A very dense  $k$ -mesh of 3333 points within the irreducible part of the Brillouin zone was used to ensure accurate results for the DOS. An optimization of the crystal structure ( $a$ ,  $y_{\text{Ge}}$ ,  $z_{\text{Ge}}$ ) for  $\text{LaPt}_4\text{Ge}_{12}$  agreed excellently with the refinement of powder X-ray diffraction data (the deviations are  $< 0.01$  Å for the Ge position and  $< 0.2\%$  for  $a$ ) emphasizing the structural stability of this system.

The calculated total DOS for  $\text{LaPt}_4\text{Ge}_{12}$  in comparison to  $\text{PrPt}_4\text{Ge}_{12}$  is plotted in Fig. 5 (upper panel). On first glance, the DOS of both compounds is very similar. The contributions of La (middle) and Pr (lower panel) to the valence band are small and featureless. The low-lying bands between  $\approx -12$  eV and  $-6$  eV are predominantly bonding Ge  $4s$  states. The majority of Pt  $5d$  states is located between  $\approx -5.5$  eV and  $-2.5$  eV and hybridizes strongly with the Ge  $4p$  orbitals. These facts support the picture of a charge transfer from the rare-earth cation to the  $[\text{Pt}_4\text{Ge}_{12}]$  polyanion. The states at  $E_F$  are mainly due to Ge  $4p$  bands. At

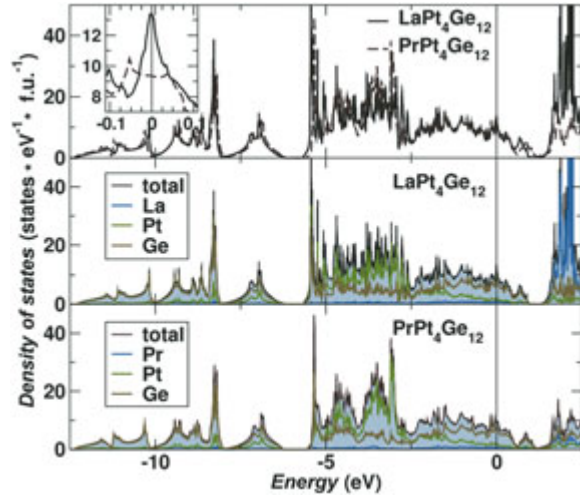


Fig. 5: Total (upper panel) and atom-resolved electronic density of states for  $\text{LaPt}_4\text{Ge}_{12}$  and  $\text{PrPt}_4\text{Ge}_{12}$ . The inset in the upper panel shows the well-pronounced peak in  $\text{LaPt}_4\text{Ge}_{12}$  in a narrow region around the Fermi level.

$E_F$ , the DOS values are 13.4 and 9.3 states  $\text{eV}^{-1}$  f.u. $^{-1}$  for the La and Pr compound, respectively, corresponding to coupling constants  $\lambda = (\gamma_N/\gamma_0) - 1$  of 1.4 and 2.9. This gives further evidence for strong electron-phonon coupling in  $\text{PrPt}_4\text{Ge}_{12}$ .

### Optimization of $T_c$ of $\text{BaPt}_4\text{Ge}_{12}$

The compounds  $\text{SrPt}_4\text{Ge}_{12}$  and  $\text{BaPt}_4\text{Ge}_{12}$  with the divalent cations Sr and Ba have lower  $T_c$  (about 5.0 K) compared to  $\text{LaPt}_4\text{Ge}_{12}$  [13,17]. Recently, also the isostructural  $\text{ThPt}_4\text{Ge}_{12}$  with tetravalent Th was reported to become superconducting below 4.62 K [18]. While for the La and Pr compounds electronic structure calculations reveal a pronounced peak in the DOS at  $E_F$ , for  $\text{SrPt}_4\text{Ge}_{12}$ ,  $\text{BaPt}_4\text{Ge}_{12}$ , and  $\text{ThPt}_4\text{Ge}_{12}$  a peak is found only in the close vicinity to  $E_F$ . Predominantly the itinerant Ge  $4p$  states are responsible for the low-energy spectrum of these systems, whereas the Pt  $5d$  electrons lie deep in energy, as we could recently demonstrate by photoelectron spectroscopy [19]. Thus, a partial replacement of Pt by a chemically similar metal could be a way to enhance  $T_c$ . Aliovalent substitution is expected to be more effective in changing  $T_c$  than isovalent substitution since the pressure dependence of  $T_c$  is weak for  $\text{BaPt}_4\text{Ge}_{12}$ . Hence, our detailed experiments and theoretical calculations were made for a substitution of platinum by gold [20].

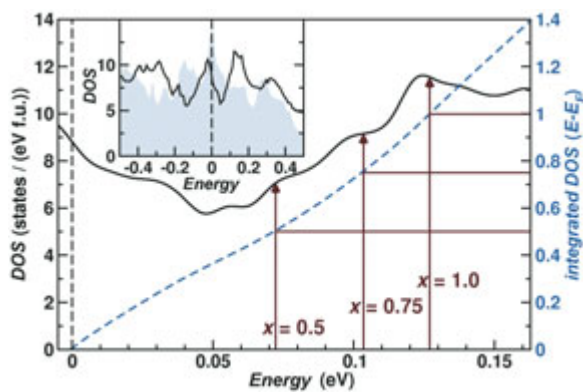


Fig. 6: Inset: electronic density of states of  $\text{BaPt}_4\text{Ge}_{12}$  (line) and  $\text{LaPt}_4\text{Ge}_{12}$  (gray area) [13]. The peak at  $E_F$  is predominantly due to Ge 4p states. Main panel: magnification of the DOS of  $\text{BaPt}_4\text{Ge}_{12}$  close to  $E_F$  (full line) and integrated DOS between  $E$  and  $E_F$  (dashed line). Arrows indicate an extra filling with 0.5, 0.75, and 1.0 electrons, respectively.

In the electronic structure calculations the substitution of Au for Pt was treated within the virtual crystal approximation (VCA). The resulting DOS for the whole valence band is very similar to that of  $\text{LaPt}_4\text{Ge}_{12}$  (Fig. 5), but shifted by a small energy. This picture suggests that the treatment within the VCA or even the rigid-band approximation should provide a reliable electronic structure. Fig. 6 shows the DOS near  $E_F$  together with its integral normalized to  $E_F$ . From the plot, the DOS can directly be obtained as function of Au content. After a drop in the DOS for  $x < 0.35$  we find a strong increase with a maximum close to  $x = 1$ . Together with the observed rigid-band-like behavior this suggests a sizable increase of  $T_c$  for  $x = 1$  assuming a constant electron-phonon coupling.

Single-phase samples exist for gold substitutions up to  $x = 1$  whereby the unit cell volume increases by 1.0% only. Magnetic susceptibility as well as specific heat measurements were used to map out the superconducting phase diagram. Both data sets show an increase of  $T_c$  from 5.0 K for  $x = 0$  to 7.0 K for  $x = 1$ . While the increase of the lattice parameter  $a$  is linear in  $x$ ,  $T_c$  increases nonlinearly and most strongly for  $x > 0.5$ . For  $x = 0.25$  almost no increase in  $T_c$  is observed.

The analysis of specific heat data showed only a small increase of the Debye temperature  $\Theta_D$  ( $\approx 4\%$ ) with the substitution of one Pt atom by Au since these atoms have almost the same mass. However, the Sommerfeld coefficient  $\gamma_N$  of  $47.3 \text{ mJ mol}^{-1} \text{ K}^{-2}$  for  $x = 0$  increases by  $\approx 20\%$  for

the compound with  $x = 1$  while  $\Delta c_p/T_c$  increases stronger. Since  $\Delta c_p/(\gamma_N T_c)$  is only 1.03 and 1.37, respectively, as compared with the weak-coupling BCS value 1.43, this may hint to a complex (multi-gap) superconducting Fermi surface. Low-temperature measurements of  $c_p(T, H)$  and of the penetration depth are underway to explore this possibility. The upper critical fields  $\mu_0 H_{c2}(0)$  extrapolated from electrical resistivity data  $\rho(T, H)$  amount to 2.0 T for both compounds, in spite of the higher  $T_c$  of the “optimized”  $\text{Ba}(\text{Pt}_3\text{Au})\text{Ge}_{12}$  material. Further research will concentrate on the low-temperature properties of rare-earth platinum skutterudites.

In summary, this selection of recent findings demonstrates that in the field of “classical” pnictogen-based filled skutterudites and, even more, of novel compounds with a germanium transition-metal framework exiting new chemical physics is waiting to be explored.

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