Superconductivity in the Platinum Germanides MPt_4Ge_{12} (M = Rare-Earth or Alkaline-Earth Metal) with Filled Skutterudite Structure

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New germanium-platinum compounds with the filled-skutterudite crystal structure were synthesized. The crystal structure and composition were investigated by x-ray diffraction and microprobe analysis. Magnetic susceptibility, specific heat, and electrical resistivity measurements evidence superconductivity in $LaPt_4Ge_{12}$ and $PrPt_4Ge_{12}$ below 8.3 K. The parameters of the normal and superconducting states were established. Strong coupling and a crystal electric field singlet ground state 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 $SrPt_4Ge_{12}$ and $BaPt_4Ge_{12}$.

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Because of a 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 and interframework interactions and are, moreover, accessible to tuning. For the skutterudites they range from magnetic and quadrupole ordering to heavy-fermion and non-Fermi liquids, itinerant ferromagnetism, half-metallicity, and good thermoelectric properties [1–4]. One of the most intriguing observations is the appearance of conventional [5–7] and heavy-fermion superconductivity in both families of cage compounds [8] with T_c up to 17 K [9,10].

The generic class of "skutterudites" derives from the archetypal mineral skutterudite $CoAs_3$. The general formula of filled skutterudites is $M_yT_4X_{12}$, 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) or a mixture of the elements of groups 14 and 16. The cations M reside in icosahedral cages formed by tilted $[TX_6]$ octahedra with interoctahedral 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 [1,11]. The binary skutterudites of cobalt group elements are diamagnetic semiconductors with a valence electron count of 72 per $[T_4X_{12}]$ 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 iron-group metal-pnicogen skutterudites the d^5-configuration of T^{3+} is not any more sufficient, and cations have to be embedded. The structure motif becomes stabilized for $NaFe_4Sb_{12}$ already with 70 electrons per f.u. [11]. The resulting electron deficiency induces metallicity associated with paramagnetism and in some cases collective magnetism [1–3].

These facts suggest a 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 the pnicogen atoms by elements of the 14th or 16th group [12,13]; (iii) by substituting the transition-metal. The interest in germanium-based clathrates and the promising applications of these framework structures [14,15] motivated us to search for chemically compatible compounds which might be accessible to semiconductor technologies.

In this Letter we report on the synthesis of the new skutteruditelike compounds MPt_4Ge_{12} composed of germanium and, for electronic balance reasons, platinum as a transition metal. They accommodate La and Pr as well as other cations (e.g., M = Sr, Ba, Ce, Nd, Eu) [16]. We examined the basic structural features through x-ray powder diffraction (XRD) and electron probe microanalysis (EPMA). Thermodynamic and transport properties were determined. We observe superconductivity with transition temperatures T_c of 8.3 K for $LaPt_4Ge_{12}$ and—unexpectedly high—7.9 K for $PrPt_4Ge_{12}$ containing $4f$ electrons. Our data are supported by band structure calculations. Though $SrPt_4Ge_{12}$ and $BaPt_4Ge_{12}$ are also superconducting we describe in detail only the two most prominent superconductors.

Samples were prepared by standard techniques. Elements in stoichiometric amounts were arc-melted on a copper hearth under Ar atmosphere. 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 $La_yPt_4Ge_{12}$ 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. Heat capacity was determined by a relaxation-type method on a PPMS (Quantum Design). Electrical resistivity data (ac, $\nu = 13.4$ Hz) were collected with a nominal current density of 0.06 $\mathrm{A\,mm^{-2}}$ in 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(3) K (La), 7.92(3) K (Pr), 5.40(8) K (Sr), and 4.98(10) K (Ba). The onsets of the transitions of the samples of the latter two compounds are broader than those with rare-earth cations and samples with lower T_c could also be observed. This indicates a large sensitivity of these compounds to subtle variations in the stoichiometry, especially to the Ba/Sr content. While shielding by supercurrents comprises the whole sample volume (zero-field cooled curves, considering the demagnetizing factor of a sphere and the high porosity of the samples) the field-cooling Meissner effect is 1 order of magnitude lower than full flux expulsion. A very small Meissner effect is well known to be due to strong pinning. The normal-state susceptibilities of the Sr, Ba, and La compounds are diamagnetic at high temperatures. The inset of Fig. 1 shows the paramagnetic susceptibility of $\mathrm{PrPt_4Ge_{12}}$. Normal-state M/H tends to saturation below ≈30 K indicating a nonmagnetic 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 Pr^{3+} ($4f^2$) with the $^3H_4$ CEF ground multiplet. The isostructural compounds $\mathrm{NdPt_4Ge_{12}}$ [$a = 8.6074(3)$ Å, Nd^{3+}] and $\mathrm{EuPt_4Ge_{12}}$ [$a = 8.6363(4)$ Å, Eu^{2+}] with magnetic CEF ground states are not superconducting above 0.48 K and display antiferromagnetic order at 0.67 and 1.7 K, respectively [16], in spite of stronger antiferromagnetic interactions (i.e., for $M =$ Eu, $\theta_P = -18.4$ K for $\mu_0 H = 0.01$ T from a low-T Curie-Weiss fit). The compound $\mathrm{CePt_4Ge_{12}}$ [$a = 8.6156(5)$ Å] exhibits fluctuating valence and no magnetic order above 0.48 K.

TABLE I. $M\mathrm{Pt_4Ge_{12}}$ compounds: structure type $\mathrm{LaFe_4P_{12}}$; space group $Im\bar{3}$; $Z = 2$. Lattice parameter a at 295 K. T_c (midpoint of transition) and the other parameters of the superconducting state were derived from specific heat. Residual or room-temperature electrical resistivity $\rho_0/\rho_{300\,\mathrm{K}}$; estimated inaccuracy due to contact geometry is ±15%.

M	a [Å]	T_c [K]	γ_N [J/mol K^2]	$\frac{\Delta c_p}{\gamma_N T_c}$	$\frac{2\Delta}{k_B T_c}$	ρ_0 [$\mu\Omega$ cm]	$\rho_{300\,\mathrm{K}}$
La[a]	8.6235(3)	8.27	0.0758	1.49	1.94	5.3	177
Pr[b]	8.6111(6)	7.91	0.0871	1.56	2.35	2.6	110
Sr	8.6509(5)	≈5.4	0.0399	1.13	···	50	239
Ba	8.6838(5)	≈5.0	0.0340	1.17	···	36	191

[a] La in $2a$ 0,0,0; Pt in $8c$ $\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$; Ge in $24g$ 0, 0.6443(3), 0.8479(3).

[b] Pr in $2a$ 0,0,0; Pt in $8c$ $\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$; Ge in $24g$ 0, 0.6401(2), 0.8475(2).

The specific heats of the two compounds with the highest T_c ($\mathrm{LaPt_4Ge_{12}}$ and $\mathrm{PrPt_4Ge_{12}}$) in various magnetic fields are presented in Fig. 2. The normal-state specific heat of $\mathrm{LaPt_4Ge_{12}}$ is well described by a model previously applied to other filled-skutterudite compounds [17–19]. The results of these fits suggest that—similar as in [$\mathrm{Fe_4Sb_{12}}$]-based skutterudites—the La atom's vibrations can be described by a low-energy Einstein term while the polyanionic host [$\mathrm{Pt_4Ge_{12}}$] is treated by the 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, Einstein temperature $\Theta_E = 96$ K for the cation, and the Sommerfeld coefficient $\gamma_N = 76\ \mathrm{mJ\,mol^{-1}\,K^{-2}}$. For $\mathrm{PrPt_4Ge_{12}}$ the values are $\Theta_D = 198$ K and $\gamma_N = 87\ \mathrm{mJ\,mol^{-1}\,K^{-2}}$ (Θ_E cannot be determined due to the CEF contribution of Pr). $\Theta_D = 198$ K for Sr and 209 K for $\mathrm{BaPt_4Ge_{12}}$ are similar (Table I lists further results).

The jumps in c_p/T at T_c were determined by an entropy-conserving construction. $\Delta c_p/\gamma_N T_c$ is 1.49 for $\mathrm{LaPt_4Ge_{12}}$ and 1.56 for $\mathrm{PrPt_4Ge_{12}}$. While this ratio indicates a coupling slightly stronger than in BCS theory ($\Delta c_p/\gamma_N T_c = 1.426$) for $\mathrm{LaPt_4Ge_{12}}$, the Pr compound is clearly a strong coupling superconductor. Comparing the electronic specific heat $c_{eS}(T)$ for $H = 0$ at $T_c/T = 2$ with the α-model [20] 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 $\mathrm{PrPt_4Ge_{12}}$.

The temperature dependence of the upper critical field H_{c2} was determined from the midpoints of the jumps in $c_p(T, H)$. The results (Fig. 2 inset) suggest that $\mu_0 H_{c2}$ varies almost linearly with T. Electrical resistivity data

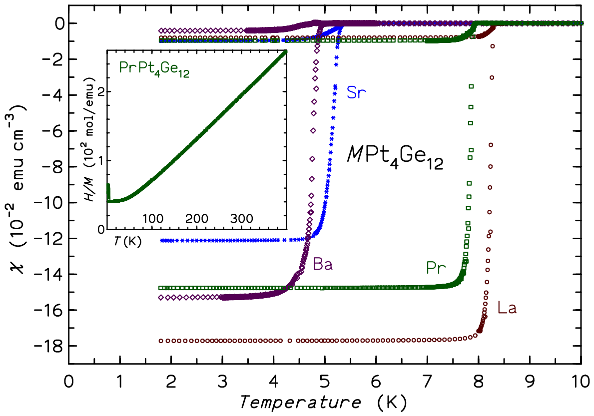

FIG. 1 (color online). Magnetic susceptibility $\chi(T)$ of filled skutterudites $M\mathrm{Pt_4Ge_{12}}$ ($M =$ Sr, Ba, La, Pr) for $\mu_0 H = 2$ mT (nominally). The inset shows the inverse molar susceptibility H/M of the Pr compound for $\mu_0 H = 1$ T.

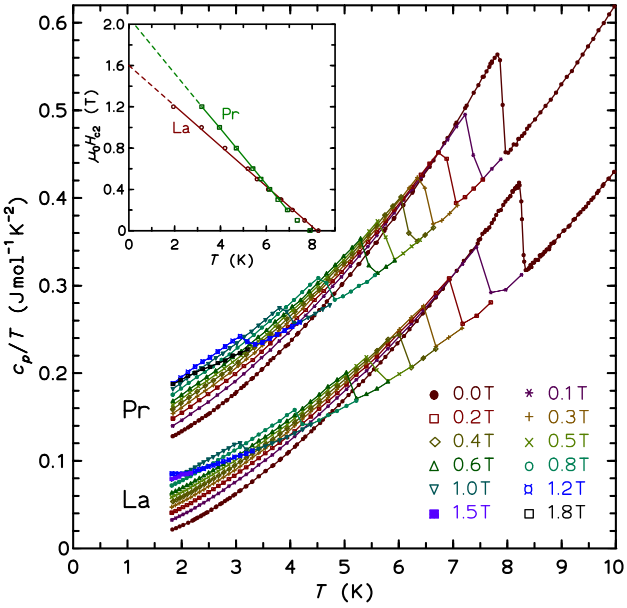

FIG. 2 (color online). Molar specific heat c_p/T of $LaPt_4Ge_{12}$ and $PrPt_4Ge_{12}$ (shifted upwards by 0.1 units) for different magnetic fields. The inset shows the critical fields H_{c2} derived from the midpoints of the transitions in $c_p(T, H)$.

(Fig. 3) confirm this finding. It is obvious from the zero-resistance points of the curves that $T_c(H)$ varies linearly with H. An extrapolation (Fig. 2 inset) yields $\mu_0H_{c2}(0) = 1.60$ T for $LaPt_4Ge_{12}$ and 2.06 T for $PrPt_4Ge_{12}$.

The residual resistivities ρ_0 of the current porous polycrystalline samples are surprisingly low ($\rho_{300\,\mathrm{K}}/\rho_0 = 33$ for $M =$ La and 42 for $M =$ Pr), indicating good sample quality. 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 $\mu_0H = 9$ T (+23% at 4 T; +9% at 2 T) just above T_c. $PrPt_4Ge_{12}$ displays similar values (+83% in 9 T). In contrast, $\rho_{300\,\mathrm{K}}/\rho_0 \approx 5$ only for our $Sr/BaPt_4Ge_{12}$ samples.

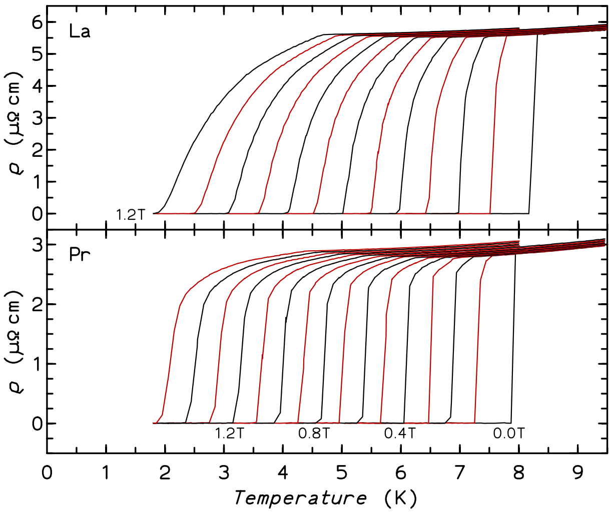

FIG. 3 (color online). Electrical resistivity of $LaPt_4Ge_{12}$ (La) and $PrPt_4Ge_{12}$ (Pr) in magnetic fields with $\Delta\mu_0H$ of 0.1 T.

The presence of superconductivity in a compound containing paramagnetic rare-earth ions is usually destroyed by pair breaking. The CEF leading to a nonmagnetic ground state in $PrPt_4Ge_{12}$ can be estimated in two ways. First, by calculating the excess specific heat $c_{\mathrm{CEF}}(T)$ with respect to the La compound. c_{CEF} can be fitted with a Schottky anomaly with an energy level scheme for the $^3H_4$ multiplet on a site with cubic point symmetry $T_h(m3)$ [21]. Secondly, the paramagnetic susceptibility can be approximated with an LLW model (for O_h symmetry) [21]. Because of the small $4f$ contribution to $c_p(T)$ the latter method seems to result in more reliable level splittings. Invariably, we find the Γ_1 singlet as ground state and the $\Gamma_4^{(1)}$ (in T_h notation) triplet at $\Delta E/k_B = 131(2)$ K. The higher levels depend sensitively on the LLW parameters. The best fit of the $4f$ contribution of $\chi(T)$ is obtained for $x = -0.85$ and $W = 5.38$, resulting in the nonmagnetic doublet Γ_{23} at 226 K and the triplet $\Gamma_4^{(2)}$ at 295 K. The well-isolated nonmagnetic CEF ground state of the Pr obviously leaves the superconductivity in $PrPt_4Ge_{12}$ almost undisturbed. This is not the case in the pnictide-based skutterudites which have significantly larger lattice parameters a. For $PrRu_4Sb_{12}$ with a $\Gamma_4^{(1)}$ first exited 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) [22]. Both superconductors were reported to show strong coupling. Other La and Pr-filled superconducting skutterudites are $La/PrRu_4As_{12}$ with T_c of 10.3 and 2.33 K, respectively [21]. For $La_xRh_4P_{12}$ T_c up to 17 K is found while the corresponding Pr compound has only a T_c of 2.4 K [9,10]. The remarkably high T_c of the "Van Vleck superconductor" $PrPt_4Ge_{12}$ and the low magnetic ordering temperatures of the Nd and Eu compounds merit further investigation.

To study the electronic structure of $La(Pr)Pt_4Ge_{12}$ a full-potential nonorthogonal local-orbital calculation scheme [23] within the local density approximation was applied. In the full-relativistic calculations, the exchange and correlation potential of Perdew and Wang [24] was used. As the basis set, La($5s, 5p, 6s, 6p, 5d, 4f$), Pr ($5s$, $5p$, $6s$, $6p$, $5d$), Pt ($5s$, $5p$, $6s$, $6p$, $5d$), and Ge ($3d$, $4s$, $4p$, $4d$) states were employed. All lower-lying states were treated as core states [25]. 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 (DOS) information, especially in the region close to the Fermi level ε_F. An optimization of the cubic crystal structure [a, y(Ge), z(Ge)] for $LaPt_4Ge_{12}$ resulted in very good agreement with the powder refinement (the deviation is <0.01 Å for the Ge position and <0.2% for a) emphasizing the structural stability of this system.

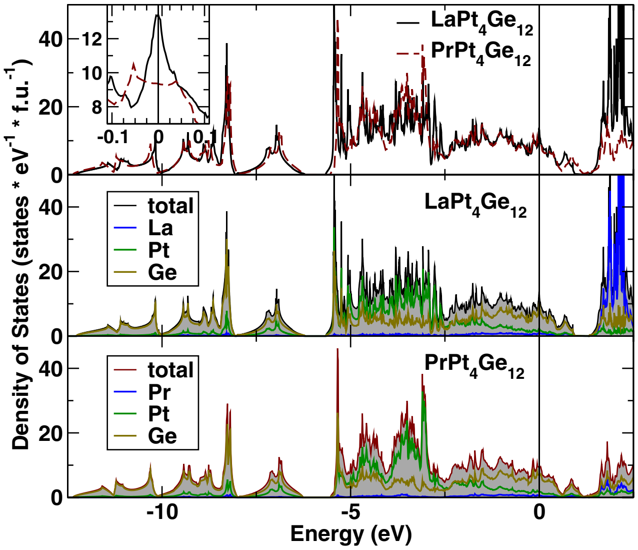

FIG. 4 (color online). Total (upper panel) and atom resolved electronic density of states for $LaPt_4Ge_{12}$ and $PrPt_4Ge_{12}$. The inset in the upper panel shows the well-pronounced peak in $LaPt_4Ge_{12}$ in a narrow region around the Fermi level.

The calculated total DOS for $LaPt_4Ge_{12}$ in comparison to $PrPt_4Ge_{12}$ is plotted in Fig. 4 (upper panel). On first glance, the 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 ≈ -12 eV and -6 eV are predominantly bonding Ge $4s$ states. The majority of Pt $5d$ states is located between ≈ -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 $[Pt_4Ge_{12}]$ polyanion. The states at ε_F are mainly (about 80%) due to Ge $4p$ bands. At ε_F the DOS values are 13.4 and 9.3 states eV^{-1} $f.u.^{-1}$ for the La and the Pr compound, respectively, corresponding to coupling constants $\lambda = \gamma_N/\gamma_0 - 1$ of 1.4 and 2.9. This gives further evidence for the considerably stronger coupling in the $PrPt_4Ge_{12}$.

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 $PrPt_4Ge_{12}$ and a nonstandard variation of H_{c2} with temperature. During revision of the paper we learnt that the compounds Sr and $BaPt_4Ge_{12}$ and their superconducting properties were recently also discovered by Bauer *et al.* [26].

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