

## Optimization of the superconducting transition temperature of the filled skutterudite $\text{BaPt}_4\text{Ge}_{12}$ by gold substitution

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The dependence of the superconducting properties of  $\text{BaPt}_4\text{Ge}_{12}$  upon substitution of platinum by gold is investigated. Full-potential electronic structure calculations suggest that the electronic density of states and the critical temperature of superconductivity  $T_c$  increases with gold content. This is confirmed by experiments. Single phase samples of  $\text{BaPt}_{4-x}\text{Au}_x\text{Ge}_{12}$  with  $x \leq 1$  are synthesized. The structural properties, magnetization, specific heat, and electrical resistivity in magnetic fields are probed. As predicted,  $T_c$  increases significantly from 5.0 K ( $x=0$ ) to 7.0 K ( $x=1$ ).

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Since its discovery, superconductivity and the systematic study of compounds showing this phenomenon represent an important topic of solid-state physics and chemistry. The improvement of the superconducting properties, in particular the critical temperature  $T_c$  and the upper critical field  $H_{c2}$ , is also a major key for the technical applications of superconducting materials.

Historically, the search for new superconductors and their improvement was largely directed by empirical concepts such as the famous Matthias rules.<sup>1</sup> On the other hand, especially in the last two decades, improved electronic structure calculations have provided an in-depth understanding of the microscopic origin of the superconducting properties for many new compounds. The theoretical electronic structure approach culminated in the case of  $\text{MgB}_2$ , where within a few years an almost complete microscopic understanding of the system has been achieved. A standard way of modifying a superconducting material is the partial substitution of one of its components. These modifications are usually directed toward the enhancement of  $H_{c2}$  or the improvement of flux line pinning. Unfortunately, in conventional superconductors  $T_c$  usually drops upon substitution caused by atomic disorder.

Recently, a new family of superconducting skutterudites  $\text{MPt}_4\text{Ge}_{12}$  ( $M=\text{Sr}, \text{Ba}, \text{La}, \text{Pr}$ ) has been reported ( $M=\text{Sr}, \text{Ba}$ <sup>2,3</sup> and  $M=\text{La}, \text{Pr}$ <sup>3</sup>). Interestingly,  $\text{PrPt}_4\text{Ge}_{12}$  with trivalent Pr in a nonmagnetic crystal field ground state has a  $T_c$  of 7.9 K, almost as high as that of  $\text{LaPt}_4\text{Ge}_{12}$  ( $T_c=8.3$  K). The compounds with divalent cations Sr and Ba have lower transition temperatures around 5.0 K.<sup>2,3</sup> Very recently, the isostructural  $\text{ThPt}_4\text{Ge}_{12}$  was reported to become superconducting below 4.62 K.<sup>4</sup>

While for the La and Pr compounds electronic structure calculations reveal a pronounced peak in the electronic density of states (DOS) at the Fermi level  $E_F$ , for  $\text{SrPt}_4\text{Ge}_{12}$  and  $\text{BaPt}_4\text{Ge}_{12}$  a peak is found only in the close vicinity to  $E_F$ . A more specific analysis of the electronic states shows that predominantly itinerant Ge 4*p* states are responsible for the low-energy spectrum of these systems, whereas the Pt 5*d* electrons lie rather deep in energy and do not contribute significantly to the aforementioned peak. This is different from the situation in the superconducting rare-earth transition-metal borocarbides,<sup>5</sup> where a similar peak in close vicinity of  $E_F$  is dominated by transition-metal contributions.

As a consequence, partial substitution of the transition metal in the latter materials did not improve their  $T_c$ .<sup>6</sup> In contrast, in  $\text{BaPt}_4\text{Ge}_{12}$  a partial replacement of Pt by a chemically similar metal could be a promising way to enhance  $T_c$ . Aliovalent substitution, thus changing the total number of electrons, is expected to be more effective in changing  $T_c$  than isovalent substitution since the dependence of  $T_c$  on pressure is reported to be weak for  $\text{BaPt}_4\text{Ge}_{12}$ .<sup>7</sup> Here, we report the results of a comprehensive study of gold substitution in  $\text{Ba}(\text{Pt}_{4-x}\text{Au}_x)\text{Ge}_{12}$ .

Samples were prepared by melting the elements in glassy carbon crucibles using a high-frequency furnace.<sup>3</sup> The samples were annealed in sealed Ta tubes in evacuated quartz ampoules at 800 °C ( $x=0$ ), 700 °C ( $x=0.25-0.75$ ), and 600 °C ( $x=1-2$ ), respectively, and then quenched in cold water. All samples were characterized by powder x-ray diffraction on a HUBER G670 imaging plate Guinier camera equipped with a Ge monochromator and Cu  $K\alpha_1$  radiation ( $\lambda=1.54056$  Å). Phase analysis was performed using the WINXPOW program package.<sup>8</sup> Lattice parameters were refined by least-squares fitting of powder data with the WINCSD program package.<sup>9</sup> All samples were metallographically characterized and the chemical composition was analyzed by wavelength dispersive electron probe microanalysis (EPMA). Small amounts of elemental Ge are the only impurity phase in samples with  $x \leq 1$ .

Resistivity measurements were carried out in a four point configuration using an ac resistance bridge (Linear Research LR700) and a current of 100  $\mu\text{A}$  perpendicular to the magnetic field. Heat capacity was measured by a relaxation-type method. Temperatures in the range  $0.35 \text{ K} < T < 300 \text{ K}$  and magnetic fields  $\mu_0 H \leq 9 \text{ T}$  were provided by a commercial measurement system (PPMS, Quantum Design). Magnetization data were determined on a superconducting quantum interference device (SQUID) magnetometer (MPMS, Quantum Design) after zero-field cooling (ZFC) and during field cooling (FC).

Electronic structure calculations within the local density approximation (LDA) of DFT were employed using the full-potential local-orbital code FPLO (version 5.00–19; Ref. 10) to estimate the optimal electron count for the Pt substitution. In the full-relativistic calculations, the exchange and correlation potential of Perdew and Wang<sup>11</sup> was used. As the basis

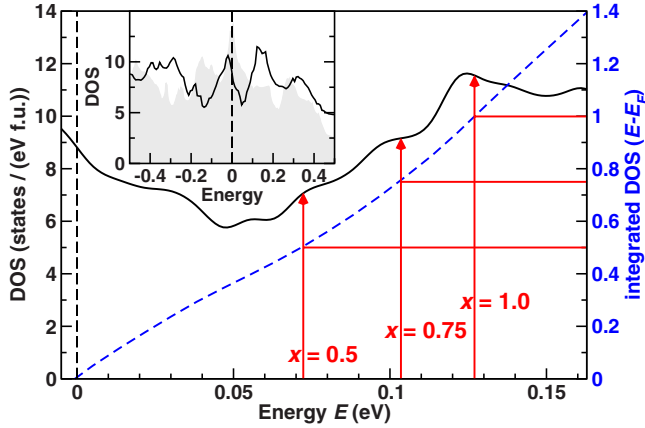


FIG. 1. (Color online) Inset: Electronic density of states of  $\text{BaPt}_4\text{Ge}_{12}$  (line) and  $\text{LaPt}_4\text{Ge}_{12}$  (gray area, Ref. 3). The peak at  $E_F$  is predominantly due to Ge  $4p$  states. Main panel: Magnification of the DOS of  $\text{BaPt}_4\text{Ge}_{12}$  close to  $E_F$  (full line) and integrated DOS between  $E$  and  $E_F$  (dashed line). Arrows indicate an extra filling with 0.5, 0.75, and  $1.0e^-$ , respectively.

set,  $\text{Ba}(5s, 5p, 6s, 6p, 5d, 4f)$ ,  $\text{Pt}(5s, 5p, 6s, 6p, 5d)$ , and  $\text{Ge}(3d, 4s, 4p, 4d)$  states were employed. Lower-lying states were treated as core. A very dense  $k$  mesh of 1256 points in the irreducible part of the Brillouin zone ( $30 \times 30 \times 30$  in the full zone) was used to ensure accurate DOS information, especially close to  $E_F$ . The substitution of Au for Pt was treated within the virtual crystal approximation (VCA).

The resulting electronic DOS for the whole valence band is very similar to that of  $\text{LaPt}_4\text{Ge}_{12}$  (see Fig. 4 of Ref. 3), but shifted by a small energy. For the region close to  $E_F$ , this is shown in the inset of Fig. 1. This picture suggests that the treatment of partial Au substitution for Pt within the VCA or even the rigid-band approximation should provide a reliable electronic structure. The VCA calculations for  $x=0.25, 0.5, 0.75$ , and  $1.0$  indeed yield DOSs close to  $E_F$  that agree almost perfectly in terms of a rigid-band shift according to the additional electrons provided by gold. This can be understood from the large and similar binding energy of Pt and Au  $5d$  states in this compound. Because of its excellent agreement with the VCA (see Table I), the rigid-band approximation is used in the following since it provides a very intuitive understanding for the electronic structure changes upon Au substitution. Figure 1 shows the fine-resolved 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 in  $T_c$  for  $x=1$  assuming a constant electron-phonon coupling.

XRD data demonstrate that single-phase samples exist for gold substitutions up to  $x=1$ . The sample with  $x=1.25$  could not be obtained as a single-phase material. For  $x \geq 1.25$  the lattice spacing  $a$  does not change further indicating a solubility limit of Au at  $x \approx 1.2$  at the applied annealing temperatures. The unit cell volume increase from  $x=0$  to  $x=1$  amounts to 1.0% only. It has to be mentioned that depending on the annealing conditions slight variations of  $a$  have been observed. For this study, a series of equally treated samples was selected.

Magnetic susceptibility data in low fields  $\mu_0 H = 2$  mT in ZFC and FC mode indicate transitions to the superconducting phase with temperatures  $T_c^{\text{mag}}$  as listed in Table I. Occasionally, a second, much smaller diamagnetic transition with  $T_c$  up to 0.6 K higher than the main transition was observed in the ZFC curve of samples with  $0 < x < 1$ . For the samples with  $x=0, 0.5, 0.75$ , and  $1.0$  heat capacity was measured in several fields and the results are depicted in Fig. 2. Both data sets show a strong increase in  $T_c$  from 5.0 K for  $x=0$  to 7.0 K for  $x=1$  [ $T_c^{\text{cal}}$  values from  $c_p(T)$ , cf. Table I]. While the increase in the lattice spacing  $a$  is linear in  $x$ , the  $T_c$  increases nonlinearly and most strongly for  $x \geq 0.5$ . For  $x=0.25$  almost no increase in  $T_c$  is observed.

The steplike (second order) phase transitions observed in  $c_p(T)$  were analyzed by fitting the data around  $T_c$  (typically  $\pm 1.5$  K) with a BCS or a two-fluid model.<sup>12</sup> The resulting relative “jump”  $\Delta c_p/T_c$  and  $T_c^{\text{cal}}$  are given in Table I. The normal state specific heat (data taken in a field of 2.0 T) is analyzed in the temperature range 3–8 K by fitting to  $c_p(T) = \gamma_N T + \beta T^3$ , where  $\gamma_N$  is the Sommerfeld electronic specific heat coefficient and  $\beta T^3$  the Debye approximation for the lattice contribution.  $\gamma_N$  and the initial Debye temperature  $\Theta_D$  as calculated from  $\beta$  are given in Table I.  $\Theta_D$  increases only little ( $\approx 4\%$ ) with the substitution of one Pt atom by Au since these atoms have almost the same mass. An increase in  $\Theta_D$ , i.e., a hardening is observed for  $M[\text{Fe}_4\text{Sb}_{12}]$  filled skutterudites with increasing electron transfer from the cation to the polyanion, but more important

TABLE I. Cubic lattice parameter  $a$  and parameters of the superconducting state of  $\text{BaPt}_{4-x}\text{Au}_x\text{Ge}_{12}$ .  $T_c^{\text{mag}}$  is defined as the crossing of the tangent to the steepest slope of the FC transition with  $\chi=0$ .  $T_c^{\text{cal}}$  is the midpoint of the jump  $\Delta c_p(T)/T_c$  with the width given in percent of  $T_c$ . For  $\gamma_N$  and  $\Theta_D$ , see text.  $\chi_0$  is the high-field susceptibility at  $T=0$ , and DOS is the electronic density of states from LDA calculations for  $x=0$  in rigid-band (RB) approach and in VCA approach.

$x$	$a$ (Å)	$T_c^{\text{mag}}$ (K)	$T_c^{\text{cal}}$ (K)	$\Theta_D$ (K)	$\gamma_N$ (mJ mol <sup>-1</sup> K <sup>-2</sup> )	$\Delta c_p/T_c$	Width (%)	$\chi_0$ (10 <sup>-6</sup> emu/mol)	DOS (RB) (states eV <sup>-1</sup> f.u. <sup>-1</sup> )	DOS (VCA)
0.00	8.6835(3)	4.98	5.03	215	47.3	48.5	1.4	-100	8.8	8.8
0.25	8.6895(5)	5.05						-170	7.0	7.0
0.50	8.6943(4)	5.27	5.19	218	49.1	55.0	0.4	-130	7.0	6.9
0.75	8.6985(4)	6.27	6.25	217	48.1	70.4	0.6	-30	9.1	9.0
1.00	8.7124(3)	7.00	7.03	224	56.3	77.0	0.2	+10	11.5	10.8

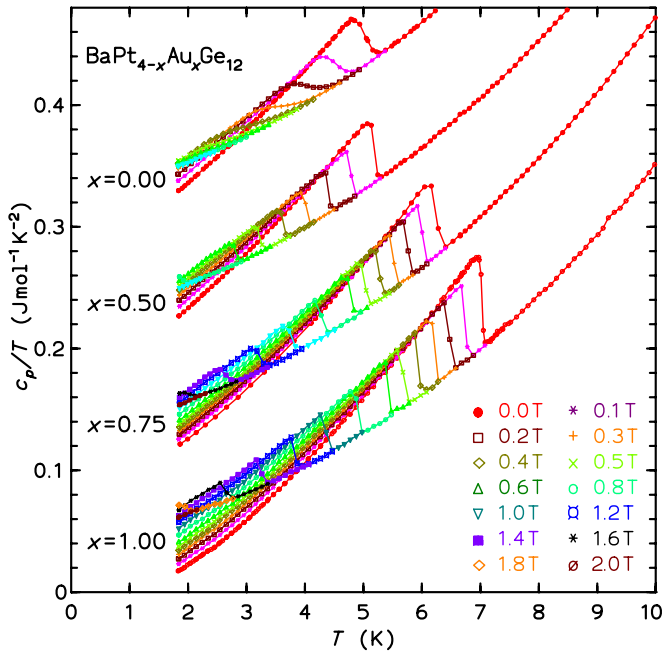


FIG. 2. (Color online) Specific heat  $c_p/T$  vs  $T$  for  $\text{BaPt}_{4-x}\text{Au}_x\text{Ge}_{12}$  in various magnetic fields. For clarity, the data for  $x=0.75$  are shifted upwards by 0.1 units, for  $x=0.5$  by 0.2 units, and those for  $x=0.0$  by 0.3 units.

in this respect is the systematic variation of physical properties of the  $M[\text{Fe}_4\text{Sb}_{12}]$  skutterudites with the charge transfer.<sup>13</sup> A similar concept seems to work also in the Pt-

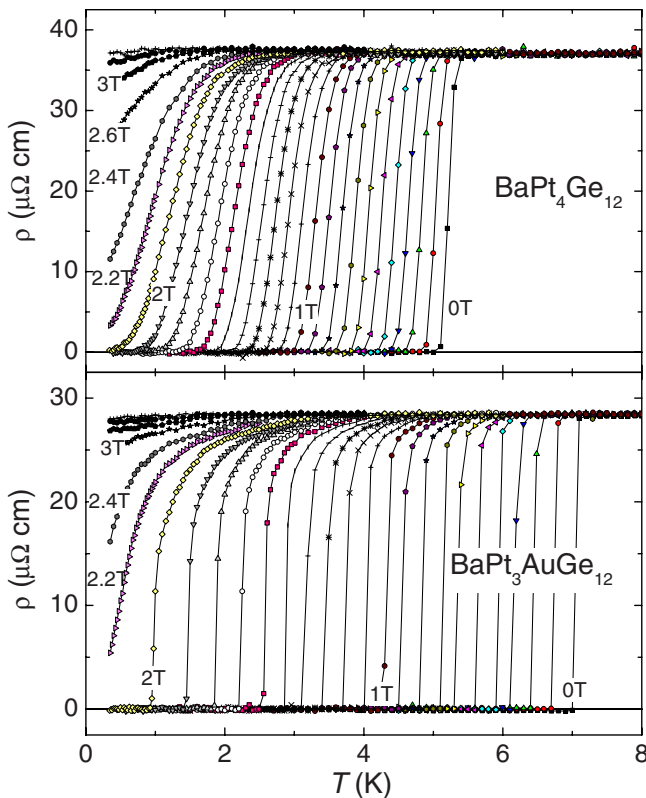


FIG. 3. (Color online) Electrical resistivity  $\rho(T, H)$  of  $\text{BaPt}_{4-x}\text{Au}_x\text{Ge}_{12}$  in magnetic fields.

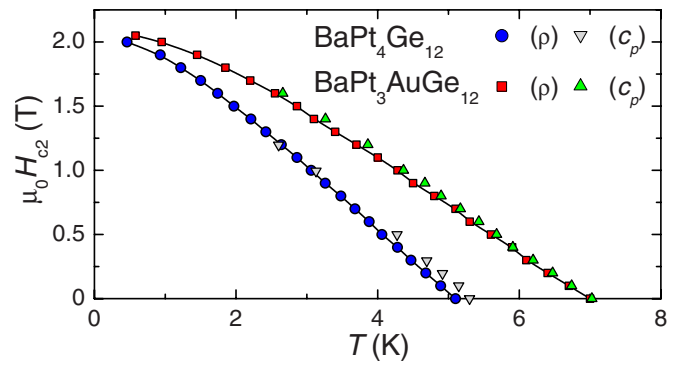


FIG. 4. (Color online) Upper critical field  $H_{c2}$  of  $\text{BaPt}_{4-x}\text{Au}_x\text{Ge}_{12}$  vs temperature determined from different properties.  $H_{c2}$  data for  $\text{BaPt}_4\text{Ge}_{12}$  from  $c_p$  are taken from Ref. 2.

based skutterudites, here however, it determines the superconducting  $T_c$ . The comparatively lower  $T_c$  of  $\text{ThPt}_4\text{Ge}_{12}$  with tetravalent thorium and the DOS calculated by similar methods for this compound<sup>4</sup> is consistent with our DOS for  $\text{BaPt}_4\text{Ge}_{12}$  in a rigid-band picture (Fig. 1 inset), i.e., hole doping by partial substitution of Pt by Ir should increase the DOS and thus  $T_c$  of the Th compound.

The Sommerfeld coefficient  $\gamma_N$  of  $47.3 \text{ mJ mol}^{-1} \text{ K}^{-2}$  for  $\text{BaPt}_4\text{Ge}_{12}$  is larger than previously reported.<sup>2,3</sup>  $\gamma_N$  increases by  $\approx 20\%$  while  $\Delta c_p/T_c$  increases stronger when comparing the compounds to  $x=0$  and  $x=1$ . Since  $\Delta c_p/(\gamma_N T_c)$  is only 1.03 and 1.37, respectively, as compared to the weak-coupling BCS value of 1.43, this may hint to a complex (multigap) superconducting Fermi surface. Low-temperature measurements of  $c_p(T, H)$  and penetration depth are underway to explore this possibility. Nevertheless, the ratio  $\Delta c_p/(\gamma_N T_c)$  increases continuously with  $x$ , which in a one-band scenario would indicate an increase in the coupling.

The temperature and field dependence of the electrical resistivity  $\rho(T, H)$  at  $T_c$  is given in Fig. 3. While the resistive transitions for  $x=0$  show a rounded foot above zero resistance, no such behavior is seen for  $x=1$ . This indicates chemical inhomogeneities as already seen in the width of the specific heat jump. For the determination of the upper critical

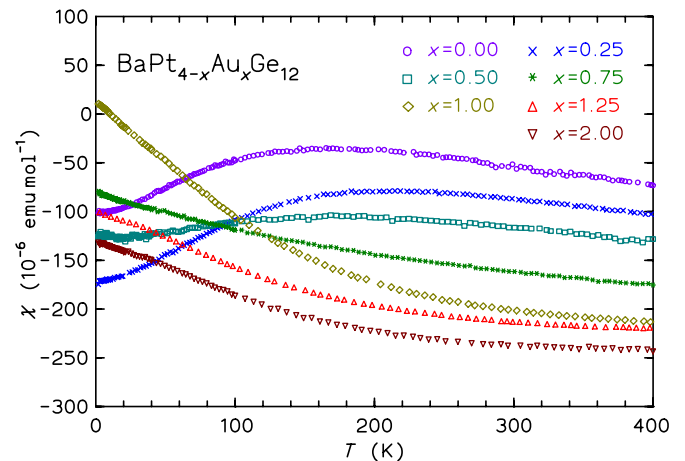


FIG. 5. (Color online) High-field ( $\mu_0 H = 7 \text{ T}$ ) magnetic susceptibility for  $\text{BaPt}_{4-x}\text{Au}_x\text{Ge}_{12}$  with different  $x$ .

field  $H_{c2}$  the zero-resistance temperatures  $T_{c,0}$  are taken. Figure 4 shows the variation of  $H_{c2}$  with temperature. For both  $x=0$  and  $x=1$  a remarkably linear variation of  $H_{c2}(T/T_c)$  for high reduced temperatures is observed. The extrapolated  $\mu_0 H_{c2}(0)$  of both compounds amounts to 2.0 T in spite of the higher  $T_c$  of the compound with  $x=1$ . The value of  $H_{c2}(0)$  and the field dependence for  $x=0$  is similar to previous observations,<sup>2</sup> where  $\mu_0 H_{c2}(0)=1.8$  T was derived.

High-field magnetic susceptibility data (Fig. 5) display a temperature dependence which changes systematically with gold content  $x$ .  $\chi(T)$  is the sum of  $T$ -independent core contributions  $\chi_{\text{core}}$  (very similar for Pt and Au) and a weakly  $T$ -dependent Pauli susceptibility  $\chi_{\text{Pauli}}(T)$ . Looking first for the zero- $T$  value  $\chi_0$  (see Table I), for  $x=0.25$  a value lower by  $60 \times 10^{-6}$  emu/mol than  $\chi_0(x=0)$  is seen, while for  $0.25 < x \leq 1$  a strong increase in  $\chi_0$  is found.  $\chi_0(x=1)$  is  $110 \times 10^{-6}$  emu/mol larger than  $\chi_0(x=0)$ . For  $x > 1$  the  $\chi_0$  again decreases. This variation is consistent with that of the DOS at  $E_F$ : from the variation of  $\chi_0(x)$  an increase in the DOS by  $\approx 3.4$  states/eV is derived within the free electron model, in good agreement with the LDA calculations (2.9 states/eV). Due to the enhancement the variation of the DOS with  $x$  is not mirrored in  $\gamma_N$ , which increases continuously with  $x$  but weaker than expected from the DOS. The clear increase in  $\Delta c_p/(\gamma_N T_c)$  may indicate a stronger coupling for  $x=1$  than for  $x < 1$ .

Looking now at the temperature dependence,  $\chi(T)$  increases with  $T$  and goes through a maximum for  $x=0$  and  $x=0.25$ . For  $x=0.5$  the susceptibility is almost  $T$  independent

and for  $0.75 \leq x \leq 1.25$  it decreases with  $T$  and becomes constant at high  $T$ . The temperature dependence of  $\chi_{\text{Pauli}}$  is determined by the DOS( $E_F$ ) and its first and second derivative.<sup>14</sup> Numerical derivation of calculated DOS data is not feasible due to limited energy resolution and smoothness. The positive quadratic rise of  $\chi(T)$  for  $x=0.25$  — a composition which is close to a DOS minimum — is however understandable.

In conclusion, we have predicted from DFT calculations that a substitution of platinum by gold, i.e., by electron doping of the skutterudite host structure, will increase the density of states and thus the superconducting  $T_c$  of  $\text{BaPt}_{4-x}\text{Au}_x\text{Ge}_{12}$  for  $x$  between 0.35 and 1.0. The prediction was experimentally confirmed by magnetization, specific heat, and electrical resistivity measurements. An increase in  $T_c$  from 5.0 K to 7.0 K and an increase in  $\Delta c_p/(\gamma_N T_c)$  is observed. Thus, the maximum  $T_c$  of the  $\text{BaPt}_{4-x}\text{Au}_x\text{Ge}_{12}$  system with one additional electron is only little lower than for the compounds with trivalent La or Pr cations. We have shown that due to the low-lying Pt 5d states the rigid-band picture is a good approximation for the band structure of this group of skutterudites. It suggests that the charge on the polyanion  $[\text{T}_4\text{X}_{12}]$ , adjusted either by electron transfer from a suitable cation  $M$  or by internal substitution, is determining the physical properties of these compounds.

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