Cage-forming compounds such as zeolites, fullerenes, clathrates or skutterudites have been proven not only of scientific but also of significant technological interest. The ability of these materials to accommodate guest filler species constitutes a wide range of varying chemical and physical properties, comprising magnetic order, heavy fermion behavior, Fermi - and non-Fermi liquid features, or conventional or unconventional superconductivity (SC). For recent reviews regarding the superconducting properties of these classes of materials see Ref. [1, 2, 3]. Most impressive, however, is the exceptional thermoelectric performance in some of the clathrates and skutterudites [4].

A structural-chemical description classifies skutterudites as cage compounds. The simple structure, however, acts as a prototype for a large class of compounds including binary as well as ternary and higher order representatives. Hitherto, cage forming elements of skutterudites entirely formed by Ge-atoms. Below $T_c = 5.35 \text{ K}$, and $5.10 \text{ K}$ for BaPt$_4$Ge$_{12}$ and SrPt$_4$Ge$_{12}$, respectively, electron-phonon coupled superconductivity emerges, ascribed to intrinsic features of the Pt-Ge framework, where Ge-$p$ states dominate the electronic structure at the Fermi energy.

Parameters were checked by EMPA and x-ray diffraction. Bulk properties of these novel skutterudites were obtained by a number of standard techniques, details are summarized in Ref [5]. Density functional theory (DFT) was applied using the Vienna $ab$ initio simulation package (VASP) [6, 7] with a fully relativistic spin-orbit coupling approach [8, 9]. The Brillouin zone was sampled with $5 \times 5 \times 5$ Monkhorst-Pack $\vec{k}$-point grids. The exchange-correlation functional was treated within the local density approximation.

The crystal structure of {Sr, Ba}Pt$_4$Ge$_{12}$ was determined from Kappa-CCD single crystal X-ray data and found to be cubic, isotypic with the filled skutterudite type LaFe$_4$Sb$_{12}$ [10]. Structure and lattice parameters are collected in Table I. Occupation factors were refined, corresponding to a full occupancy of the Pt and Ge sub-lattices. Although not revealed from single crystal refinement, minor deviations (up to 3 %) from full occupancy are possible for the Ba and Sr atoms. Since the size of the Ge-framework is significantly smaller than the corresponding Sb-framework, effective bonding between the framework cages (two icosahedra per unit cell) and the Ba(Sr)-center atoms is ensured. As a consequence of this stronger bond between cage and guest atom, we observe very regular thermal atom displacement factors (ADP) on all atoms. The temperature dependencies of ADPs in the temperature region from 100 to 300 K reveal for all atoms similar trends: typical rattling modes caused by the heavy guest atoms in Sb-based skutterudites are absent in {Ba, Sr}Pt$_4$Ge$_{12}$. The structural parameters as derived from DFT calculations are in excellent agreement with the experimental data. In order to analyze the thermodynamical stability of XPt$_4$Ge$_{12}$ (X=Ba, Sr) compounds we also calculated the total energy for a hypothetical compound Pt$_4$Ge$_{12}$. The bonding energy $E_X$ for guest atom X is obtained from the relation $E_X = U_{XPT_4Ge_{12}}^{DFT} - U_{Pt_4Ge_{12}}^{DFT} - U_X^{DFT}$ in which $U_X^{DFT}$ denotes the corresponding total energy of the compound or elemental solid in its equilibrium state. The values $E_{Ba} = -3.24 \text{ eV}$ and $E_{Sr} = -3.38 \text{ eV}$ emphasize the stabilizing effect of the Ba and Sr guest atoms.

Superconductivity in novel Ge-based skutterudites: {Sr, Ba}Pt$_4$Ge$_{12}$

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Combining experiments and $ab$ initio models we report on SrPt$_4$Ge$_{12}$ and BaPt$_4$Ge$_{12}$ as members of a novel class of superconducting skutterudites, where Sr or Ba atoms stabilize a framework entirely formed by Ge-atoms. Below $T_c = 5.35 \text{ K}$, and $5.10 \text{ K}$ for BaPt$_4$Ge$_{12}$ and SrPt$_4$Ge$_{12}$, respectively, electron-phonon coupled superconductivity emerges, ascribed to intrinsic features of the Pt-Ge framework, where Ge-$p$ states dominate the electronic structure at the Fermi energy.

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Superconductivity is found for BaPt$_4$Ge$_{12}$ and SrPt$_4$Ge$_{12}$ from resistivity measurements using polycrystalline samples at $T_c \approx 5.3$ K and 5.1 K, respectively (compare Fig. 1(a,b)). The normal state regions, $T > T_c$ of these ternary compounds do not behave like simple metals, since the standard model of the electrical resistivity of metallic systems, i.e., the Bloch-Grüneisen formula is not applicable. Such observations were made in many superconducting materials and may be attributed to a substantial electron-phonon interaction strength, responsible for the formation of Cooper pairs in conventional superconductors. Rather, the overall $\rho(T)$-dependence of both skutterudites follows the model of Woodward and Cody [1], which initially was applied to A15 superconductors such as Nb$_3$Sn. Least squares fits to this model are shown as solid lines in both figures, revealing reasonable agreement for characteristic temperatures $T_0 = 123$ and 121 K, respectively. The differences of the residual resistivities may correspond to small differences in the filling of the 2(a)-sites by Ba or Sr. In case of the smaller atom Sr, filling seems to be more complete. The application of a magnetic field suppresses superconductivity of BaPt$_4$Ge$_{12}$ at fields above 2 T, while for SrPt$_4$Ge$_{12}$ the upper critical field $H_{c2}(0) \approx 1$ T (insets of Fig. 1).

The susceptibility $\chi$ exhibits a rather sharp transition at $T = 5.3$ and 5.1 K [inset, Fig. 2(b)], dropping from an initially small positive value to the diamagnetic value of $-1/(4\pi)$ for zero field cooling, which corresponds to a full Meissner Ochsenfeld effect. Magnetization measurements performed at various temperatures and magnetic fields up to 6 T evidence type II superconductivity. Upper critical field values are summarized in Fig. 3.

The heat capacity, $C_p$, of \{Sr,Ba\}Pt$_4$Ge$_{12}$ is plotted in Fig. 2 as $C_p/T$ vs. $T$ for zero and 3 T. For sake of clarity, measurements taken at intermediate field values are not shown here. The jump of $C_p(T)$ below 6 K evidences bulk superconductivity in both cases. An idealization of the heat capacity anomaly under the constraint of entropy balance between the superconducting and the normal state yields $T_c = 5.35$ and 5.1 K for the Ba and Sr based compounds, respectively. Assuming that the specific heat of metallic compounds at low temperature follows $C_p = \gamma T + \beta T^3$, ($\gamma$ is the Sommerfeld coefficient and $\beta$ is proportional to the Debye temperature $\theta_D$), least squares fits reveal $\gamma = 42$ mJ/molK$^2$ and $\beta_D = 247$ K (Ba) and $\gamma = 41$ mJ/molK$^2$ and $\beta_D = 220$ K (Sr). It is worth to be noted that the Debye temperature of BaPt$_4$Ge$_{12}$ is larger than that of SrPt$_4$Ge$_{12}$. In general, however, materials with smaller masses exhibit larger Debye temperatures. This anomaly observed may correspond to the fact that, while the volume of the unit cells of both compounds differ by only 1%, the atomic volumes of Sr and Ba differ by about 12%. This causes a weaker bonding of Sr to the framework, hence a weaker force constant may result in lower values of $\theta_D$.

![FIG. 1: (Color online) Temperature dependent electrical resistivity $\rho$ of BaPt$_4$Ge$_{12}$ (a) and SrPt$_4$Ge$_{12}$ (b). Both insets show the field dependence of $\rho(T)$.](image)

![FIG. 2: (Color online) (a) Temperature dependent specific heat $C_p$ of SrPt$_4$Ge$_{12}$ and BaPt$_4$Ge$_{12}$ plotted as $C_p/T$ vs. $T$ for 0 and 3 T. (b) Semi-logarithmic plot $C_p/T$ vs. $T_c/T$. The inset shows the low temperature and low field susceptibility $M/H$ for both compounds.](image)

| TABLE I: Normal state and superconducting properties of BaPt$_4$Ge$_{12}$ and SrPt$_4$Ge$_{12}$ which crystallize in the cubic skutterudite structure: space group Im3, (No. 204); Ba and Sr are at the 2(a) (0, 0, 0) sites, Pt at the 8(c) $\{\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\}$ sites, and Ge at the 24g (0, y, z) sites. $U_{eq}$ is a mean value of the atomic displacement ellipsoid. |
|---|---|---|
| property | BaPt$_4$Ge$_{12}$ | SrPt$_4$Ge$_{12}$ |
| lattice parameter $a$ @300 K [nm] | 0.86928(3) | 0.86601(3) |
| Ce 24g site: y | 0.15302 | 0.15197 |
| Ge 24g site: z | 0.35683 | 0.35536 |
| $R_{F2} = \sum |F_{2}^0|^2 - \sum |F_{2}^0| \sum |F_{2}^0|$ | 0.019 | 0.018 |
| $U_{eq}(\text{Ba, Sr})$ [nm$^2$] | 0.000066(2) | 0.000118(3) |
| $U_{eq}(\text{Pt})$ [nm$^2$] | 0.000062(1) | 0.000069(1) |
| $U_{eq}(\text{Ge})$ [nm$^2$] | 0.000092(2) | 0.000097(2) |
| transition temperature $T_c$ [K] | 5.35 | 5.10 |
| upper critical field $\mu_0H_{c2}$ [T] | 1.8 | 1 |
| thermodyn. critical field $\mu_0H_c$ [mT] | 53 | 52 |
| Fermi velocity $v_F$ [m/s] | 52500 | 67000 |
| coherence length $\xi$ [nm] | 14(1) | 18(1) |
| penetration depth $\lambda$ [nm] | 320(10) | 250(10) |
| G.L. parameter $\kappa$ | 24(1) | 14(1) |
Taking into account the McMillan model [12] allows calculation of the dimensionless electron-phonon coupling constant $\lambda$. Setting the repulsive screened Coulomb term $\mu^* \approx 0.13$, yields in both cases $\lambda \approx 0.7$. This refers to superconductors well beyond the weak coupling limit. In comparison, $\mu^*$ of different cage forming compounds covers a range from $\approx 0.1$ to $\approx 0.3$ [1-2,3].

The jump of the specific heat $\Delta C_p/T (T = T_c) \approx 58 \text{mJ/molK}^2$ (Ba) and $\approx 57 \text{mJ/molK}^2$ (Sr) allows calculation of $\Delta C_p/(\gamma T_c) \approx 1.35$, which is near to the figure expected from BCS theory $[\Delta C_p/(\gamma T_c) \approx 1.43]$. As the magnetic field strength increases (not shown here), both the transition temperature and the anomaly right at $T_c$ are suppressed, constituting the phase diagram in Fig. 3.

The superconducting gap $\Delta(0)$ can be derived from a comparison of the modified BCS expression, $C_{cs}(T) = 8.5 \gamma T_c \exp(-0.82\Delta(0)/k_B T)$ with the experimental data depicted in a semi-logarithmic plot $C_{cs}/\gamma T_c$ vs. $T_c/T$ in Fig. 2(b) where BaPt$_4$Ge$_{12}$ and SrPt$_4$Ge$_{12}$ exhibit for $T_c/T > 2$ an exponential temperature dependence indicating a ratio $\Delta(0)/k_B T_c \approx 1.8$ in close agreement with the BCS value $\Delta_{BCS}(0) = 1.76 k_B T_c$.

The thermodynamic critical field is calculated from the free energy difference between the superconducting and normal state: $\Delta F(T) = F_n - F_s = \mu_0 H_{c2}^2(T)/2$, where $F_n$ and $F_s$ are evaluated from the specific heat in the normal and superconducting state, respectively. The values obtained are $\mu_0 H_{c2}(0) \approx 53 (2)$ and $52 (2)$ mT for Ba and the Sr-based compound, respectively.

Fig. 3 displays the temperature dependent upper critical field $\mu_0 H_{c2}$ of {Sr, Ba}Pt$_4$Ge$_{12}$ as deduced from field dependent resistivity, magnetization, and heat capacity measurements. The slopes of the upper critical field $\partial(\mu_0 H_{c2})/\partial T \equiv \mu_0 H_{c1}'$ are collected in Table I yielding slightly larger values deduced from magnetization and resistivity data than those from specific heat, which may be attributed to pinning and surface effects. $\mu_0 H_{c2}$ of BaPt$_4$Ge$_{12}$ is larger than $\mu_0 H_{c2}$ of SrPt$_4$Ge$_{12}$.

Primarily, two mechanisms are responsible for the limited value of $\mu_0 H_{c2}$: orbital pair breaking and Pauli limiting. Werthamer et al. [13] derived an expression ($WHH$ model) for the upper critical field $\mu_0 H_{c2}$ in terms of orbital pair-breaking, including the effect of Pauli spin paramagnetism and spin-orbit scattering. A comparison of the experimental results with the WHH model is based on two parameters, $\alpha$, the Pauli paramagnetic limitation ($Maki$ parameter) and $\lambda_{so}$ describing spin-orbit scattering. If the atomic numbers of the elements constituting the material increase, $\lambda_{so}$ is expected to increase as well.

The Maki parameter $\alpha$ can be estimated via the Sommerfeld value $\gamma$ and $\rho_0$ [13], i.e., $\alpha = (3e^2h\gamma\rho_0)/(2m^2\pi^2k_B^2)$ with $e$ the electron charge and $m$ the electron mass. Taking the experimental $\rho_0$ and $\gamma$ yields $\alpha = 0.18$ for BaPt$_4$Ge$_{12}$ and $\alpha = 0.14$ for SrPt$_4$Ge$_{12}$. We have adjusted the WHH model to the experimental data (dashed and dashed-dotted lines in Fig. 3), revealing $\lambda_{so} \approx 15$ for all data-sets.

The thermodynamic and the upper critical field are used to calculate the ratio of the penetration depth $\lambda_{GL}(0)$ to the coherence length $\xi_{GL}(0)$ via Abrikosov’s relation $\lambda_{GL}(0)/\xi_{GL}(0) \equiv \kappa_{GL}(0) = H_{c2}/[\sqrt{2}H_c(0)]$ yielding the Ginzburg-Landau parameter $\kappa_{GL} = 24 (2)$ and $14 (2)$ for the Ba and Sr-based compounds. The absolute values of the coherence length $\xi_0$ and the penetration depth $\lambda(0)$ can be calculated via the isotropic Ginzburg-Landau-Abrikosov-Gor’kov (GLAG) theory. Values obtained are presented in Table I.

The Fermi velocity $v_F$ can be calculated from the Fermi surface area $S_F$ as shown by Orlando et al. [14]. Values are given in Table I. Combining $S_F$ and $\rho_0$, a mean free path $l_{tr}$ of about $\approx 1.0 \cdot 10^{-5}$ m and $\approx 1.4 \cdot 10^{-5}$ m for the Ba and Sr compound, respectively, is derived.

The fact that $\mu_0 H_{c2}$ of BaPt$_4$Ge$_{12}$ is larger than that of SrPt$_4$Ge$_{12}$ can be understood in terms of the Ginzburg-Landau theory. Hake [15] and Orlando et al. [14] derived a model equation for $\mu_0 H_{c2}$ which primarily depends on two parameters: on the inverse of the square of $v_F$ and on the inverse of $l_{tr}$. Taking into account the parameters deduced from the above analyses explains in both cases, at least qualitatively, differences of $\mu_0 H_{c2}^2$. While the decrease of $v_F$ from the Sr to the Ba case can be perceived by an increase of the unit cell volume ($v_F \propto (N/V)^{1/3}$, for free electrons), the decrease of the mean free path corresponds to the increase of the residual resistivity from SrPt$_4$Ge$_{12}$ to BaPt$_4$Ge$_{12}$.

From $l_{tr}/\xi \approx 1$ we classify {Ba, Sr}Pt$_4$Ge$_{12}$ as a dirty limit superconductor, and $\kappa$ of the order of 10 to 20 refers to a pronounced type II superconducting behavior.

The DOS in Fig. 4 reveal the individual contributions of $X=$ {Ba, Sr}, Pt and Ge atoms showing that Ge states, which are of $p$–like character, are dominating at Fermi energy. The Ge states hybridize with Pt $5d$–like states by which the spin-orbit coupling effect is transmitted to the
obvious among pnictogen-based skutterudites. The metallic features of the DOS around E_F are being deduced. The metallic features of the DOS around E_F convincingly confirm that the Zintl concept no longer applies to {Sr, Ba}Pt_4Ge_{12}, while its applicability is quite obvious among pnictogen-based skutterudites. The total DOS at E_F can be compared with the Sommervell value of the specific heat γ = \frac{1}{2} \pi^2 N(E_F) k_B^2. The experimental values slightly larger than 40 mJ/molK^2 for the Ba and Sr compounds, along with an electron-phonon enhancement factor \lambda_p = 0.7 (estimated via the McMillan formula \[12\]) would require a bare DOS equivalent to \approx 25 mJ/molK^2, which compares favorably with the DOS calculations involving spin-orbit coupling: 31 mJ/molK^2 for the Ba (N(E_F) = 13.2 states eV^{-1} f.u^{-1}) and 28 mJ/molK^2 for the Sr compound (N(E_F) = 12.1 states eV^{-1} f.u^{-1}). Without spin-orbit coupling, the specific heats, γ, are 19.5 and 21.0 mJ/molK^2 for Ba and Sr, respectively. This implies the importance of the relativistic effects.

In summary, superconducting {Sr, Ba}Pt_4Ge_{12} are the first skutterudites where the framework in the structure is entirely built by Ge-atoms. DFT calculations proved that X=(Ba,Sr) guest atoms strongly stabilize the compounds. Most strikingly, the calculated DOS around E_F is composed of hybridized Ge 4p-like and Pt 5d-like states, and it has a sharp peak with its maximum very close to E_F. The influence of the guest atoms (Ba or Sr) on superconductivity, however, may be ruled out due to the fact that (i) the Ba- or Sr-like DOS around E_F is negligible and (ii) the DOS around E_F for the hypothetical X-free Pt_4Ge_{12} framework is very similar to the one of XPt_4Ge_{12} (X = Ba and Sr). Hence, superconductivity appears to be an intrinsic property of the Pt-Ge cage-forming structure. This conclusion is in line with the slightly smaller value of T_c observed in SrPt_4Ge_{12}, in marked contrast to the isotope effect, where lighter masses would originate larger SC transition temperatures.

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