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 $T_c = 5.35$ and 5.10 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.

Cage-forming compounds such as zeolithes, 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 spe-
cies constitutes a wide range of varying chemical and
physical properties, comprising magnetic order, heavy fer-
mion behavior, Fermi- and non-Fermi liquid features, or
conventional or unconventional superconductivity. For re-
cent reviews regarding the superconducting properties of
these classes of materials see Refs. [1–3]. Most impressive,
however, is the exceptional thermoelectric performance in
some of the clathrates and skutterudites [4].

A structural-chemical description classifies skutteru-
dites 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 are es-
sentially based on volatile and/or toxic pnictogens ($X = P$,
As, Sb). Building blocks in the framework are eight tilted
octahedra per unit cell enclosing two icosahedral cages.
Each of the octahedra is centered by a transition metal
atom like Co or its homologues (Rh, Ir).

Motivated by the known manifold of interesting physical
properties among skutterudites, we searched for ternary
and/or higher order compounds exploiting the combination
of (i) a high density of d states of a platinum group metal at
the Fermi level with (ii) a rigid framework of rather co-
valently four-bonded atoms such as Si and/or Ge. Thereby
a novel family of Ge-based skutterudites, SrPt$_4$Ge$_{12}$ and
BaPt$_4$Ge$_{12}$, has been identified. The aim of the present
work is a study of the stability and the characterization
of bulk properties by means of resistivity, magnetization,
specific heat, and electronic structure calculations. For
both compounds, the low temperature behavior is domi-
nated by the appearance of superconductivity around 5 K.

{Sr,Ba}Pt$_4$Ge$_{12}$ samples were prepared from stoichio-
metric amounts of high purity elements by argon arc
melting and subsequently heat treated in evacuated quartz
capsules at 800 °C for two weeks. Phase purity and lattice

parameters were checked by electron microprobe analysis
and x-ray diffraction. Bulk properties of these novel skut-
terudites were obtained by a number of standard tech-
niques; 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 sublattices. Although
not revealed from single crystal refinement, minor devia-
tions (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 frame-
work, 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's) on all atoms. The tempera-
ture dependencies of ADP's 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 $E_X = U_{X\text{Pt}_4\text{Ge}_{12}}^{\text{DFT}} - U_{\text{Pt}_4\text{Ge}_{12}}^{\text{DFT}} - U_X^{\text{DFT}}$ in
which U^{DFT} denotes the corresponding total energy of
the compound or elemental solid in its equilibrium state.

TABLE I. Normal state and superconducting properties of $BaPt_4Ge_{12}$ and $SrPt_4Ge_{12}$ which crystallize in the cubic skutterudite structure: space group $Im\bar{3}$, (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	$BaPt_4Ge_{12}$	$SrPt_4Ge_{12}$
Lattice parameter a @300 K [nm]	0.869 28(3)	0.866 01(3)
Ge $24g$ site: y	0.153 02(7)	0.151 97(7)
Ge $24g$ site: z	0.356 83(6)	0.355 36(6)
$R_{F2} = \sum |F_o^2 - F_c^2| / \sum F_o^2$	0.019	0.018
$U_{eq}(\{Ba, Sr\})$ [nm^2]	0.000 066(2)	0.000 118(3)
$U_{eq}(Pt)$ [nm^2]	0.000 062(1)	0.000 069(1)
$U_{eq}(Ge)$ [nm^2]	0.000 092(2)	0.000 097(2)
Transition temperature T_c [K]	5.35	5.10
Upper critical field $\mu_0 H_{c2}$ [T]	1.8	1
Thermod. critical field $\mu_0 H_c$ [mT]	53	52
FERMI velocity v_F [m/s]	52 500	67 000
Coherence length ξ [nm]	14(1)	18(1)
Penetration depth λ [nm]	320(10)	250(10)
G.L. parameter κ	24(1)	14(1)

The values $E_{Ba} = -3.24$ eV and $E_{Sr} = -3.38$ eV emphasize the stabilizing effect of the Ba and Sr guest atoms.

Superconductivity is found for $BaPt_4Ge_{12}$ and $SrPt_4Ge_{12}$ from resistivity measurements using polycrystalline samples at $T_c \approx 5.3$ K and 5.1 K, respectively, [compare Figs. 1(a) and 1(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 [11], which initially was applied to A15 superconductors such as Nb_3Sn. Least squares fits to this model are shown as solid lines in both figures, revealing reasonable agreement

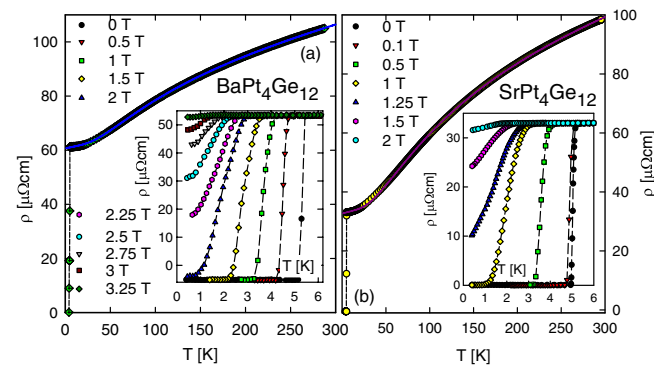for characteristic temperatures $T_0 = 123$ and 121 K, respectively. The differences of the residual resistivities may correspond to small differences in the filling of the $2(a)$ sites by Ba or Sr. In the case of the smaller atom Sr, filling seems to be more complete. The application of a magnetic field suppresses superconductivity of $BaPt_4Ge_{12}$ at fields above 2 T, while for $SrPt_4Ge_{12}$ the upper critical field $H_{c2}(0) \approx 1$ T (insets of Fig. 1).

The susceptibility χ 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 $\{Sr, Ba\}Pt_4Ge_{12}$ is plotted in Fig. 2 as C_p/T vs T for 0 and 3 T. For the 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 balanced 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 β is proportional to the Debye temperature θ_D), least squares fits reveal $\gamma = 42$ mJ/mol K^2 and $\theta_D = 247$ K (Ba) and $\gamma = 41$ mJ/mol K^2 and $\theta_D = 220$ K (Sr). It is worthwhile to note that the Debye temperature of $BaPt_4Ge_{12}$ is larger than that of $SrPt_4Ge_{12}$. In general, however, materials with smaller masses exhibit larger Debye temperatures. This observed anomaly 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;
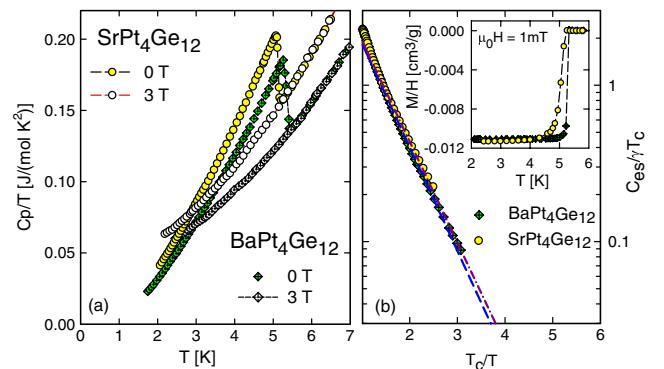

FIG. 1 (color online). Temperature dependent electrical resistivity ρ of $BaPt_4Ge_{12}$ (a) and $SrPt_4Ge_{12}$ (b). Both insets show the field dependence of $\rho(T)$.

FIG. 2 (color online). (a) Temperature dependent specific heat C_p of $SrPt_4Ge_{12}$ and $BaPt_4Ge_{12}$ plotted as C_p/T vs T for 0 and 3 T. (b) Semilogarithmic plot $C_{es}/\gamma T_c$ vs T_c/T. The inset shows the low temperature and low field susceptibility M/H for both compounds.

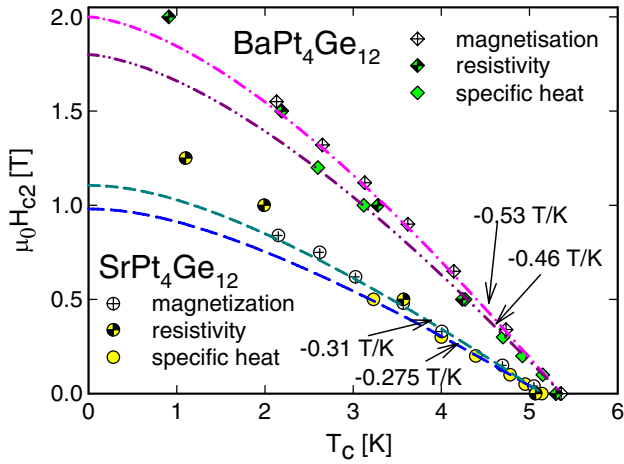FIG. 3 (color online). Temperature dependent upper critical
field $\mu_0 H_{c2}$ of BaPt$_4$Ge$_{12}$ and SrPt$_4$Ge$_{12}$ as obtained from
resistivity, magnetization, and specific heat measurements. The
dashed and the dashed-dotted lines represent the WHH model.

hence, a weaker force constant may result in lower values
of θ_D.

Taking into account the McMillan model [12] allows
calculation of the dimensionless electron-phonon coupling
constant λ. 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, μ^* of different cage-forming compounds cov-
ers a range from ≈ 0.1 to ≈ 0.3 [1–3].

The jump of the specific heat $\Delta C_p/T (T = T_c) \approx$
58 mJ/mol K^2 (Ba) and ≈ 57 mJ/mol K^2 (Sr) allows cal-
culation of $\Delta C_p/(\gamma_n T_c) \approx 1.35$, which is near 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, $C_{es}(T) =$
$8.5 \gamma T_c \exp(-0.82 \Delta(0)/k_B T)$ with the experimental data
depicted in a semilogarithmic plot of $C_{es}/\gamma T_c$ 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 indicat-
ing 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: $\Delta F(T) = F_n - F_s = \mu_0 H_c^2(T)/2$, where F_n
and F_s are evaluated from the specific heat in the normal
and superconducting state, respectively. The values ob-
tained are $\mu_0 H_c(0) \approx 53(2)$ and $52(2)$ mT for the Ba-
and the Sr-based compound, respectively.

Figure 3 displays the temperature dependent upper criti-
cal 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

$\partial(\mu_0 H_{c2})/\partial T \equiv \mu_0 H'_{c2}$ hold slightly larger values de-
duced from magnetization and resistivity data than those
from specific heat, which may be attributed to pinning and
surface effects.

Primarily, two mechanisms are responsible for the lim-
ited value of $\mu_0 H_{c2}$: orbital pair breaking and Pauli limit-
ing. Werthamer, Helfand, and Hohenberg (WHH) [13]
derived an expression 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, α, the Pauli paramag-
netic limitation (*Maki parameter*) and λ_{so}, describing spin-
orbit scattering. If the atomic numbers of the elements
constituting the material increase, λ_{so} is expected to in-
crease as well.

The Maki parameter α can be estimated via the
Sommerfeld value γ and ρ_0 [13]; i.e., $\alpha =$
$(3 e^2 \hbar \gamma \rho_0)/(2 m \pi^2 k_B^2)$ with e the electron charge and m
the electron mass. Taking the experimental ρ_0 and γ 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 ξ_0 and the penetration depth $\lambda(0)$ can
be evaluated via the isotropic Ginzburg-Landau-
Abrikosov-Gor'kov theory. Values obtained are presented
in Table I.

The Fermi velocity v_F can be calculated from the Fermi
surface area S_s as shown by Orlando *et al.* [14]. Values are
given in Table I. Combining S_s and ρ_0, a mean free path l_{tr}
of about $\approx 1.0 \times 10^{-8}$ m and $\approx 1.4 \times 10^{-8}$ 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 $\mu_0 H'_{c2}$. While the decrease of
v_F from the Sr to the Ba case can be conceived by an
increase of the unit cell volume [$v_F \propto (N/V)^{1/3}$, for free
elelctrons], 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 κ of the order of 10 to 20 refers
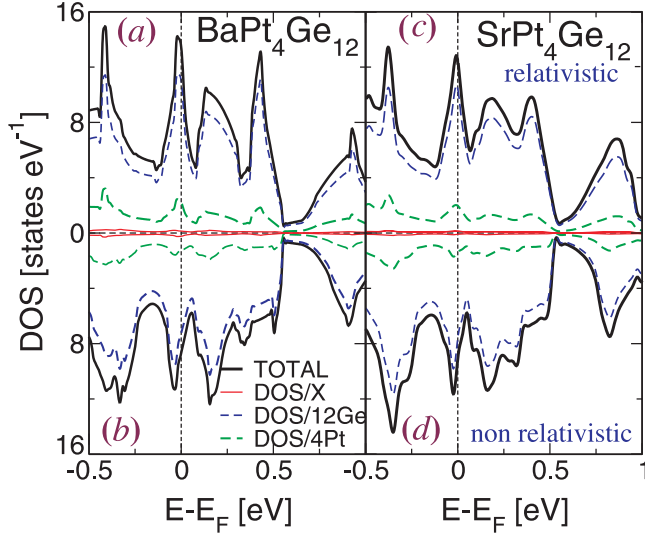to a pronounced type II superconducting behavior.

FIG. 4 (color online). DOS for $BaPt_4Ge_{12}$ (a), (b) and $SrPt_4Ge_{12}$ (c), (d) as derived from DFT calculations. Fermi energy is situated at zero energy. The upper half (a), (c) shows the density of states for a fully relativistic calculation, which includes spin-orbit coupling. The lower half (b), (d) of the figure presents the DOS of a standard nonrelativistic calculation. The total DOS is decomposed into the local DOS representative for one Ba(Sr), four Pt, and twelve Ge atoms. The relativistic effect is small but important, because it shifts the Fermi level of the nonrelativistic DOS almost into the maximum of the relativistic DOS.

The density of states (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 DOS at E_F. Consequently, by making use of the electron localization function technique [16], expressive Ge-Ge covalent bonds and typical metallic Pt bonding 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 Sommerfeld value of the specific heat $\gamma = \frac{1}{3}\pi^2 N(E_F)k_B^2$. The experimental values, being slightly larger than 40 mJ/mol K^2 for the Ba and Sr compounds, along with an electron-phonon enhancement factor $\lambda_{ep} = 0.7$ (estimated via the McMillan formula [12]) would require a bare DOS equivalent to ≈ 25 mJ/mol K^2, which compares favorably with the DOS calculations involving spin-orbit coupling: 31 mJ/mol K^2 for the Ba [$N(E_F) = 13.2$ states eV^{-1} f.u.$^{-1}$] and 28 mJ/mol K^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/mol K^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 superconductivity transition temperatures.

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