Platinum metal silicides and germanides: superconductivity in non-centrosymmetric intermetallics

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Abstract.

The family of intermetallics crystallizing in the BaAl\textsubscript{4} type is rich in sub-groups with different ordered variants. Novel ternary compounds EpTMX\textsubscript{3} (Ep = Sr,Ba; TM = Pd,Pt; X = Si,Ge) crystallizes in the body-centred tetragonal BaNiSn\textsubscript{3} structure (space group \textit{I}4\textsubscript{mm}) which does not possess a centre of inversion. Superconductivity in terms of a fully gapped \textit{s}-wave type occurs for SrPdGe\textsubscript{3} at \(T_c = 1.49\) K and SrPtGe\textsubscript{3} at \(T_c = 1.0\) K.

1. Introduction

Intermetallics with the BaAl\textsubscript{4} type are rich in sub-groups with different ordered variants. Novel ternary compounds EpTMX\textsubscript{3} (Ep = Sr,Ba; TM = Pd,Pt; X = Si,Ge) crystallizing in the body-centred tetragonal BaNiSn\textsubscript{3} structure with \(c/a \approx 2.2\) and exhibit superconductivity below 3 K. The BaNiSn\textsubscript{3} structure, space group \textit{I}4\textsubscript{mm}, does not possess a centre of inversion with respect to its \textit{c}-axis (see e.g., Ref. [1]). This causes an antisymmetric spin-orbit coupling (ASOC) and gives rise to a splitting of electronic bands which destroys the spin-degeneracy of the bands. The strength of this effect is proportional to \(Z^2\) (\(Z\) is the atomic number); hence, the ASOC may be “tuned” by increasing the element masses in the respective materials. Theoretically, the splitting of bands leads to a mixture of spin-singlet and spin-triplet components in the superconducting condensate [2]. In this study, the normal and the superconducting state of EpTMX\textsubscript{3} will be characterised experimentally, and we make use of density functional theory (DFT) calculations to provide electronic density of states (DOS) at the Fermi energy (\(E_F\)) as well as the splitting of bands along high-symmetric directions around \(E_F\). We find that the different atomic masses in the compounds modify the ASOC and the band splitting is modified as well.

2. Experimental and computational details

BaPtSi\textsubscript{3}, SrPdGe\textsubscript{3}, and SrPtGe\textsubscript{3} were prepared by arc-melting on a water-cooled copper hearth in Ti-gettered argon from elemental ingots with a minimum purity of 99.9 mass\%. All samples
were sealed in quartz tubes and annealed at 900°C for 100 h before quenching in cold water. X-ray powder diffraction and other measurements were carried out with standard techniques [5].

The DFT calculations were done by using the Vienna ab initio simulation package (VASP) utilizing the projector augmented wave construction for the pseudopotentials (Ref. [6]). The potential for Sr comprises 10 valence states including the 4s and 4p states. The Pt potential was constructed for 10 valence states, whereas for Pd also the 4p semicore states are included resulting in 16 valence states in total. For Ge 14 valence states are taken into account including the 3d states. The electronic many-body interactions were described within the local density approximation. All structural parameters were optimized with an error smaller than 1.5% as compared to experiment.

3. Results and discussion

3.1. BaPtSi₃

Recently, BaPtSi₃ as an example of a non-centrosymmetric superconductor was studied. [1] A superconducting phase transition was observed at 2.25 K in combination with an upper critical field at \( T = 0 \) K of \( \approx 0.05 \) T. Based on a BCS-like heat capacity for \( T < T_c \) a simple \( s \)-wave superconducting state was suggested. Relativistic DFT calculations revealed only a rather small splitting of bands at \( E_F \) and Fermi surface nesting features were found for two characteristic double-sets of bands [1]. Hence, superconductivity seems to appear in an almost undisturbed BCS state. To microscopically prove this conclusion, we have carried out low temperature muon spin resonance (\( \muSR \)) spectroscopy.

In this type of experiment, a field orthogonal to the muon polarisation is applied with the sample temperature above the superconducting transition temperature and then the sample is cooled. The muon response as a function of applied field and temperature provides accurate determination of the magnetic penetration depth, \( \lambda \), coherence length, \( \xi \), and also the superfluid density, \( n_s \). The results of the muon experiments are shown in Fig. 1. The inset of Fig. 1 shows the temperature dependence of the muon depolarisation rate, \( \sigma_s \), and precession frequency. The precession frequency shows a characteristic drop at \( T_c \) indicating that a vortex state has been established and that we have a type II superconductor. The \( \sigma_s \) value shows an increase at \( T_c \) which plateaus at low temperatures. The temperature dependence of \( \sigma_s \) has been fitted using the \( N \)-fluid model, \( \sigma_s = \sigma(0)(1 - (T/T_c)^N) \), which give a reasonable description to the data. The results of the fit are \( \sigma(0) = 1.10(2) \) \( \mu \)s\(^{-1} \), \( T_c = 1.75(2) \) K and \( N = 2.0(1) \). This is strongly suggestive, and confirms the heat capacity results that BaPtSi₃ is an \( s \)-wave BCS superconductor. The reduction in \( T_c \) is due to the applied field being close to \( H_{c2} \). In Fig. 1, \( \sigma_s \) shows a decrease as the applied field is increased, because the flux lines are overlapping. The data can be well described assuming a hexagonal flux line lattice [3, 4], which is usually valid for \( \kappa = \lambda/\xi > 5 \),

\[
\sigma_s = 4.83 \times 10^4 \left( 1 - \frac{\mu_0 H}{\mu_0 H_{c2}} \right) \left( 1 + 1.21 \left( 1 - \frac{\mu_0 H}{\mu_0 H_{c2}} \right)^{0.5} \right)^3 \lambda^{-2}. \tag{1}
\]

Here we find \( \lambda = 188(10) \) nm and \( \mu_0 H_{c2} = 64(3) \) mT yielding \( \xi = 72(5) \) nm. This gives \( \kappa = 2.6 \). Although this value is less than that which is normally acceptable for this model, we can see the fit to the data is good and our results are in good agreement with those reported in Ref. [1].

3.2. SrPdGe₃ and SrPtGe₃

The crystal structure data were determined by X-ray Rietveld refinement and found to be isotypic to the body-centred tetragonal BaNiSn₃ type. The lattice parameters observed are \( a = 0.44677(4) \) nm and \( c = 1.02863(10) \) nm (SrPdGe₃) and \( a = 0.44859(3) \) nm and \( c = 1.01364(8) \) nm (SrPtGe₃).
In order to characterise superconductivity occurring in EpMGe$_3$, we have carried out resistivity measurements as a function of temperature, field and pressure and we have studied the heat capacity at various externally applied magnetic fields. The resistivity in both cases shows metallic behaviour and a superconducting transition at 1.5 K (SrPdGe$_3$) and 1 K (SrPtGe$_3$). The application of external pressure reduces the $T_c$ of SrPdGe$_3$ by about 0.2 K at 20 kbar. Such a behaviour is typical for the overwhelming number of BCS superconductors. External magnetic fields rapidly suppresses superconductivity, which vanishes in both samples already at fields below a tenth of a Tesla. The fact that SrPdGe$_3$ exhibits the larger transition temperature compared to the Pt based system is in line with the lighter element Pd and follows also the trend of typical BCS superconductors.

The temperature dependent heat capacity $C_p$ of SrPdGe$_3$ and SrPtGe$_3$ is displayed in Figs. 2,3 as $C_p/T$ vs. $T$. These measurements clearly reveal bulk superconductivity in both compounds, excluding impurities as the origin of the phase transitions around at 1.5 and 1.0 K, respectively. The application of a magnetic field suppresses superconductivity for fields of the order of 0.1 T, in agreement with the resistivity data. To derive information regarding the superconducting order parameter, the BCS model calculation by Mühlschlegel is used to describe $C_p(T)$ for $T < T_c$. This model assumes $s$-wave pairing and a fully opened gap in the electronic density of states (DOS) at the Fermi energy $E_F$. The BCS model does not contain any adjustable parameter, except the superconducting transition temperature $T_c$ and the Sommerfeld coefficient $\gamma_n$, implying that the temperature dependent heat capacity is a universal function, applicable to each BCS-like superconductor. This model reveals a jump of the heat capacity at $T = T_c$ with $[\Delta C/(\gamma_n T_c)] = 1.43$. An adjustment of the transition temperature reveals $T_c = 1.49$ K for SrPdGe$_3$ and $T_c = 1.0$ K for SrPtGe$_3$. The agreement between the BCS model and the present experimental data is convincing assuming $\gamma = 5$ and 4 mJ/molK$^2$, for the Pd and Pt system, respectively and adding an impurity term of the order of 0.6 mJ/molK$^2$. The latter might be a consequence of errors in the addenda calibration of the calorimeter (PPMS, Quantum Design). The excellent agreement observed is considered as an indication of standard $s$-wave BCS superconductivity in both, SrPdGe$_3$ and SrPtGe$_3$. 

Figure 1. The field dependence of $\sigma$ at 0.1 K. The insert shows the temperature dependence of $\sigma$ and the precession frequency at 0.03 T. In both figures the solid line is a fit to the data as described in the text.

Figure 2. (a) Temperature dependent specific heat $C_p$ of SrPdGe$_3$ for various values of applied field. The solid line represents the heat capacity of an $s$-wave BCS superconductor.
Figure 3. Temperature dependent specific heat $C_p$ of SrPtGe$_3$ for various values of applied field. The solid line represents the heat capacity of an $s$-wave BCS superconductor.

Figure 4. Electronic band structure of SrPtGe$_3$ for high symmetry directions of the body-centred tetragonal crystal structure including spin-orbit interaction.

The very low values for $\mu_0H_c(0)$ (well below the Pauli limiting field of $\mu_0H > 1$ T) and the exponential temperature dependence of $C_p$ make unconventional superconductivity in SrPdGe$_3$ and SrPtGe$_3$ rather unlikely. A further indication that the lack of inversion symmetry is of negligible importance for superconductivity can be gained from the DFT relativistic band structure, which includes spin-orbit coupling (SO), as shown for SrPtGe$_3$ in Fig. 4. SO causes a sizeable splitting of degenerate bands, e.g., at the $\Gamma$-point of about 0.5 eV. Furthermore, the remaining degeneracy becomes lifted by the electric field gradient owing to the absence of inversion symmetry (compare e.g., the bands along $\Gamma - N$). Both splitting effects are absent in non-SO calculation. The splitting of bands due to the non-inversion symmetry, however, remains small, in particular at $E_F$. This might be an indication that a mixing of spin-singlet and spin-triplet components in the superconducting condensate is weak and spin-singlet Cooper pairs dominate. The electronic band structure of SrPdGe$_3$ is rather similar, but the splitting effects are less pronounced because of the smaller mass of Pd in comparison to Pt.

In summary, we have shown that body-centred tetragonal SrPdGe$_3$ and SrPtGe$_3$ are new superconductors without inversion symmetry with transition temperatures around 1.5 and 1 K, respectively. The absence of strong correlations among electrons and the minor splitting of bands favours a fully gapped $s$-wave superconducting state. A microscopic evidence for a simple superconducting state was derived for BaPtSi$_3$ from $\mu$SR studies.

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