

Structural, Electronic and Superconducting Properties of Filled Skutterudites MPt_4Ge_{12} ($M = Sr, Ba, La, Ce, Pr, Nd, Sm, Eu$)

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Skutterudites and clathrates are intermetallic compounds with cage-like structures which have been investigated at the MPI-CPfS for several years by now. New filled skutterudite compounds MPt_4Ge_{12} with a host structure composed of germanium and platinum have been discovered [1]. This novel cage structure accommodates early rare-earth ions (La, Ce, Pr, Nd, Sm, Eu) as well as the alkaline-earth ions Sr and Ba [2,3]. Meanwhile, other groups have reported isostructural compounds with $M = Th, U$ [4, 5]. The compound with $M = Sr, Ba, La, Th$, and – most interestingly – Pr are superconductors with T_c up to 8.2 K [2–4]. Recently, we have studied the structural, electronic, magnetic, and especially the superconducting properties of these compounds in depth with a wide variety of methods and within several external collaborations. In addition, further theoretical and experimental investigations were devoted to the vibrational and ferromagnetic properties of iron-antimony based filled skutterudites [6–8].

Structure and Bonding

A comprehensive study of the crystal structure and chemical bonding in MPt_4Ge_{12} provides the basis for the understanding of the physics of this class of compounds [9]. Therefore, systematic studies of the crystal structure based on single-crystal diffraction data have been carried out. Depending of the size of the M species, atomic displacement parameters of filler atoms M can be similar or much larger than those of Pt and Ge. This observation is mainly due to structural peculiarities since the electropositive metal atoms M reside in a large (distorted icosahedral) cage within the platinum-germanium framework. This trend of atomic displacement parameters has been observed in all filled skutterudite phases and has been paraphrased in the literature as “rattling” motion of M . However, our detailed lattice-dynamics calculations and experimental studies (in co-operation with scientists of the ILL, Grenoble) of the vibrational dynamics by inelastic neutron scattering in Fe-Sb-based skut-

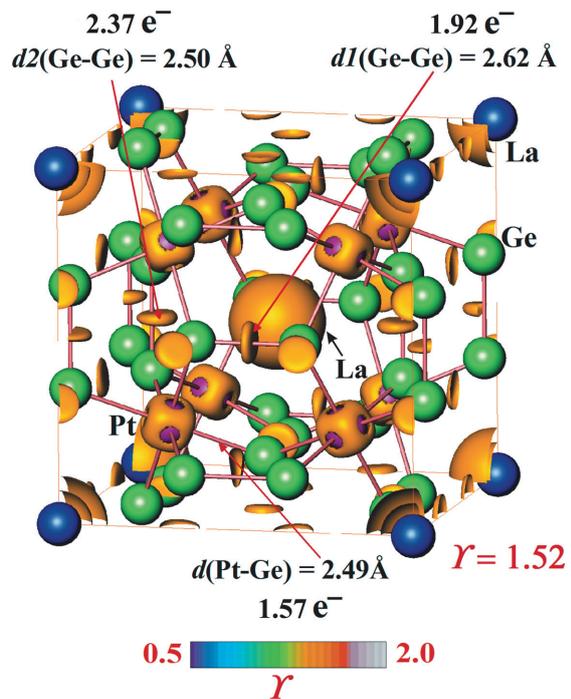


Fig. 1: Electron localizability indicator in $LaPt_4Ge_{12}$. The isosurface of ELI-D reveals a structuring of the penultimate shell of Pt (the pink sphere is the Pt nucleus) and appearance of the maxima on the Ge–Ge bonds. The maxima corresponding to the Pt–Ge bonds occur at a lower ELI-D value and therefore are not shown. The bond counts are obtained from the integration of the electron density within the basins of the ELI attractors [9].

terudites show that the vibrational DOS follows the theory of harmonic crystals and thus the common phonon-glass (electron-gas) model description is called into question [6].

Electronic structure calculations and chemical bonding analysis by the electron localizability indicator (ELI, Fig. 1) describe the MPt_4Ge_{12} compounds as covalently bonded polyanionic $[Pt_4Ge_{12}]$ framework structures which are stabilized by electron transfer from the filler cation M . The interaction involving the electrons of the penultimate shell of the M atoms is visualized. In case of filled skutterudite compounds containing $3d$ metals, the DOS at the Fermi level is dominated by contributions of

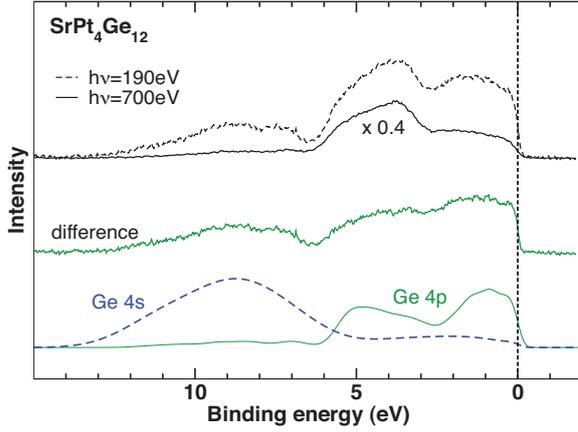


Fig. 2: Normalized and background-corrected valence-band photoemission spectra of $\text{SrPt}_4\text{Ge}_{12}$ taken with a photon energy of 190 eV (black dashed line) and 700 eV (black-solid line). The 700 eV spectrum has been rescaled with a factor of 0.4. The difference spectrum (green solid line) is compared to the calculated Ge 4p DOS (green thin line) and Ge 4s DOS (blue dashed line) [10].

3d metal states. In contrast, for the $\text{MPt}_4\text{Ge}_{12}$ compounds, it is essentially composed of Ge p states with Pt 5d contributions at significantly lower energies.

$\text{SrPt}_4\text{Ge}_{12}$ – a photo-electron spectroscopy study

For an evaluation of the electronic band structures as well as the chemical bonding analysis, spectroscopic data are desirable. Such a validation is important since one would like to know whether band theory can provide a solid basis for the modeling of the physical properties in the $\text{MPt}_4\text{Ge}_{12}$ series. We therefore set out to perform a comparative study [10] of the valence-band electronic structure of superconducting $\text{SrPt}_4\text{Ge}_{12}$ by means of X-ray photoelectron spectroscopy and full-potential band structure calculations. Excellent agreement between the measured photoemission spectra and the LDA band structure calculation was observed (Fig. 2). This agreement confirms the picture of the chemical bonding analysis yielding rather deep-lying Pt 5d states which only partially contribute to covalent bonds with the Ge 4p electrons. In turn, the states at the Fermi level that are relevant for superconductivity of this compound can be firmly assigned to originate predominantly from Ge 4p electrons.

Unconventional superconductivity in $\text{PrPt}_4\text{Ge}_{12}$

The crystal field ground state of Pr in $\text{PrPt}_4\text{Ge}_{12}$ is a Γ_1 singlet and the first excited triplet state $\Gamma_{4(1)}$ lies very high ($\Delta E \cdot k_B^{-1} \approx 130$ K) [2]. This basically allows for superconductivity with comparatively high T_c of 7.9 K for this compound ($\text{LaPt}_4\text{Ge}_{12}$: $T_c = 8.3$ K). Early on we observed that for both the La and Pr compounds [2, 11] the electronic specific heat well below T_c is proportional to T^3 instead of increasing exponentially with T . Such behavior hints at point nodes in the k -dependence of the superconducting energy gap $\Delta(k)$ [11]. A study of the superfluid density $\rho_s(T/T_c)$ down to temperatures of $0.004 T_c$ (Fig. 3a) by means of transverse-field muon spin rotation spectroscopy (μSR) in cooperation with scientists of the Paul Scherrer Institute, Switzerland, confirmed this conclusion. Moreover, the detailed temperature dependence of $\rho_s(T/T_c)$ was compared with the quasi-particle

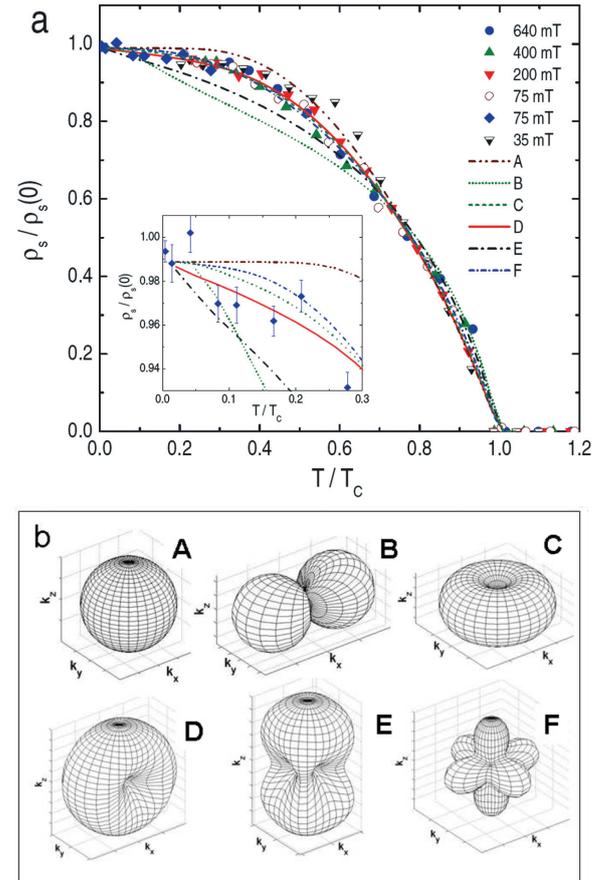


Fig. 3: Temperature dependence of the superfluid density $\rho_s(T/T_c)$ normalized to its value at $T = 30$ mK. The lines represent fits using six different models for the k -dependence of the energy gap as illustrated in the lower panel. The inset magnifies the low-temperature region [11].

spectrum resulting for diverse superconducting gap functions $\Delta(k)$ (see Fig. 3b) compatible with the T_h symmetry of the filled skutterudite crystal structure. It is evident that the isotropic BCS-type gap cannot describe the data, but models C, D, and F provide a good description of $\rho_s(T/T_c)$. Indeed, functions C and D come with a gap-to- T_c ratio $\Delta_0/k_B T_c$ of 2.68 and 2.29, respectively, which are compatible with our specific heat data, while model F can be excluded. These two gap symmetries have point nodes and have been discussed as favorable descriptions for the heavy-fermion superconductor $\text{PrOs}_4\text{Sb}_{12}$.

Further studies with μSR in zero field addressed the question of the presence of a magnetic field in the superconducting Meißner phase [12]. The presence of an internal field hints at time-symmetry breaking by a non-singlet superconducting order parameter. We were successful to detect such a signal below T_c for $\text{PrPt}_4\text{Ge}_{12}$ but not for $\text{LaPt}_4\text{Ge}_{12}$ [12], suggesting that the Pr-compound is an unconventional superconductor. In addition, we prepared samples of $\text{Pr}_x\text{La}_{1-x}\text{Pt}_4\text{Ge}_{12}$ and measured their T_c and the specific heat jump Δc_p at T_c . Interestingly, both properties do not show strong deviations from a linear variation with the substitution parameter x . This points to a compatibility of the order parameter symmetries of $\text{LaPt}_4\text{Ge}_{12}$ and $\text{PrPt}_4\text{Ge}_{12}$, which is not expected for a spin-singlet and a spin-triplet order parameter. One may thus speculate that the degeneracy of the order parameter of $\text{PrPt}_4\text{Ge}_{12}$ is within the orbital channel instead of the spin degree-of-freedom. Further μSR investigations of $\text{LaPt}_4\text{Ge}_{12}$ and of $\text{SrPt}_4\text{Ge}_{12}$ and $\text{BaPt}_4\text{Ge}_{12}$, which have lower T_c , are underway.

CePt₄Ge₁₂ – Ce on the intermediate valence side

Regarding the typical broad maximum in the magnetic susceptibility $\chi(T)$, $\text{CePt}_4\text{Ge}_{12}$ was immediately suspected to exhibit an intermediate (fluctuating) valence of cerium [2]. Furthermore, the ^{195}Pt NMR shift which probes the local susceptibility, shows a similar behavior [13]. A more in-depth study [14] by high-energy resolution fluorescence detected (HERFD) X-ray absorption spectroscopy (performed at the ESRF Grenoble) revealed a temperature-independent Ce valence close to three (Fig. 4). The electronic specific heat coefficient γ of $\text{CePt}_4\text{Ge}_{12}$ is moderately enhanced ($105 \text{ mJ mol}^{-1} \text{ K}^{-2}$), both with respect to $\text{ThPt}_4\text{Ge}_{12}$ (as reference for the tetravalent state; $\gamma =$

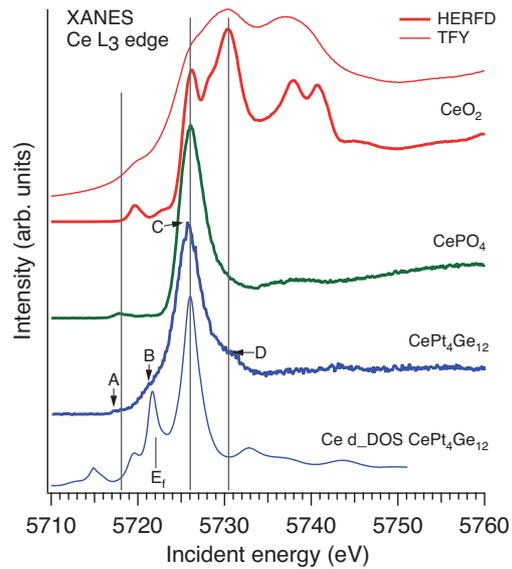


Fig. 4: Experimentally obtained high-resolution (HERFD) Ce L_{III} XANES spectra of CeO_2 , CePO_4 and $\text{CePt}_4\text{Ge}_{12}$ recorded with the X-ray emission energy set to 4839 eV at 300 K and the theoretically calculated partial density of states of $\text{CePt}_4\text{Ge}_{12}$. The spectrum of CeO_2 is compared with total fluorescence yield (TFY) curves. The Ce atoms in $\text{CePt}_4\text{Ge}_{12}$ are in a valence state close to +3 in the whole measured temperature range.

$40 \text{ mJ mol}^{-1} \text{ K}^{-2}$) and $\text{LaPt}_4\text{Ge}_{12}$ (as reference for the trivalent state; $\gamma = 76 \text{ mJ mol}^{-1} \text{ K}^{-2}$), indicating moderately enhanced band masses. An analysis of the specific-heat data [14] revealed a broad maximum of the f -electron contribution at $\approx 65\text{K}$, which coincides roughly with similar maxima in the Seebeck coefficient $S(T)$ ($+32 \mu\text{V K}^{-1}$ at 80 K) and the aforementioned maximum in the magnetic susceptibility. $\text{CePt}_4\text{Ge}_{12}$ shows Fermi-liquid behavior at low temperatures and is a metal with dominating hole-like charge carriers (as proven by Hall-effect data). Our detailed ^{195}Pt NMR study [13] (Knight shift and spin-lattice relaxation rate) is however consistent with the picture of an intermediate Ce valence. These findings are in contrast to the conclusions of another group which interprets their results in the framework of a correlated semimetal with a large number of residual states in the gap [15].

An exotic heavy fermion system – SmPt₄Ge₁₂

The $M\text{Pt}_4\text{Ge}_{12}$ skutterudites with Nd and Eu could be synthesized by conventional methods. While the Nd ion is – as usual – trivalent, and has a quartet ground state, the Eu in $\text{EuPt}_4\text{Ge}_{12}$ is in a stable (divalent) $4f^7$ configuration with the $^8S_{7/2}$ state. Both compounds order antiferromagnetically at

low temperatures ($T_N = 0.67$ K and 1.78 K, respectively) [16]. The Sm compound, however, could only be synthesized at elevated pressure (5 GPa) and is metastable at ambient conditions.

The magnetic susceptibility of $\text{SmPt}_4\text{Ge}_{12}$ is of van-Vleck type and similar to that of ionic compounds with trivalent Sm [17]. In contrast, an investigation by X-ray absorption spectroscopy resulted in a non-integer valence state of Sm ($\nu = 2.90(3)$), which is independent of temperature. This is in agreement with the deviation of the cubic lattice parameter a of $\text{SmPt}_4\text{Ge}_{12}$ from the linear relation of a vs. ionic radius of the M^{3+} ions for La, Pr, and $\text{NdPt}_4\text{Ge}_{12}$ [9].

Due to the presence of Einstein-like modes in the specific heat of both $\text{SmPt}_4\text{Ge}_{12}$ and $\text{LaPt}_4\text{Ge}_{12}$, the analysis of the $4f$ -derived contributions at elevated temperatures is complicated (Fig. 5). As in the pnictogen-based skutterudites, these Einstein modes may be related to the displacement parameter U_{iso} of the rare-earth guest obtained from diffraction data [6, 8]. Actually, the values of U_{iso} increase dramatically when going from $\text{LaPt}_4\text{Ge}_{12}$ to $\text{SmPt}_4\text{Ge}_{12}$ [9] and for the latter an Einstein temperature $\theta_E \approx 65$ K is derived from U_{iso} . Assuming the same contribution from the host for both compounds but different Einstein terms, the conduction electron and $4f$ -derived terms to $c_p(T)$ can be calculated (Fig. 5). At low T a large broad anomaly remains. A fit to the data results in a linear specific heat coefficient of $\gamma' = 450 \text{ mJ mol}^{-1} \text{ K}^{-2}$, qualifying the compound as a heavy fermion. Most remarkable, the anomaly does not change in a magnetic field of 9 T.

A similarly robust specific heat anomaly is observed for $\text{SmOs}_4\text{Sb}_{12}$. For this compound γ' is $820 \text{ mJ mol}^{-1} \text{ K}^{-2} - 880 \text{ mJ mol}^{-1} \text{ K}^{-2}$. Currently, a mechanism involving a hybridization of electronic states with the low-lying phonon mode ($\theta_E \approx 40$ K) of Sm in $\text{SmOs}_4\text{Sb}_{12}$ is discussed for such an exotic heavy fermion state [18]. We thus speculate that this scenario is also applicable for $\text{SmPt}_4\text{Ge}_{12}$, however, the hybridization should be weaker due to the higher energy of the phonon mode of Sm.

Summary and Outlook

Filled skutterudite compounds based on platinum and germanium have been investigated in depth. Our recent activities concentrate on a further clarification of the superconducting order parameter, on substitution studies, and on compounds with similar crystal structures.

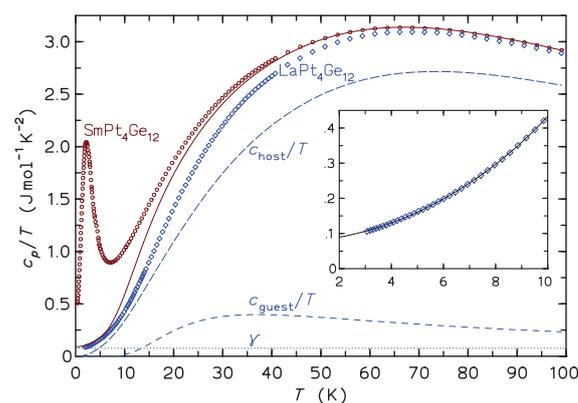


Fig. 5: Specific heat of $\text{SmPt}_4\text{Ge}_{12}$ (circles) and $\text{LaPt}_4\text{Ge}_{12}$ (diamonds) and fit (inset). $c_p(T)$ of $\text{LaPt}_4\text{Ge}_{12}$ consists of: (i) the host-structure contribution (long-dashed), (ii) the Einstein contribution of the La guest (short-dashed), (iii) the electronic contribution γT (dotted) [17].

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