Electronic structure of SrPt₄Ge₁₂: Combined photoelectron spectroscopy and band structure study


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We present a combined study of the electronic structure of the superconducting skutterudite derivative SrPt₄Ge₁₂ by means of x-ray photoelectron spectroscopy and full-potential band structure calculations including an analysis of the chemical bonding. We establish that the states at the Fermi level originate predominantly from the Ge 4p electrons and that the Pt 5d shell is effectively full. We find excellent agreement between the measured and the calculated valence-band spectra, thereby validating that band structure calculations in combination with photoelectron spectroscopy can provide a solid basis for the modeling of superconductivity in the compound series MP₄Ge₁₂ (M=Sr, Ba, La, Pr).

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I. INTRODUCTION

Compounds with crystal structures featuring a rigid covalently bonded framework enclosing differently bonded guest atoms attracted much attention in the last decade. In particular, the skutterudite and clathrate families have been investigated in depth, and a fascinating diversity of physical phenomena is observed; many of which are due to subtle host-guest interactions. Among the skutterudites, the phenomena range from magnetic ordering to heavy-fermion and non-Fermi liquids, superconductivity, itinerant ferromagnetism, half metallicity, and good thermoelectric properties.¹⁻⁴ Superconductivity of conventional⁵⁻⁷ and heavy-fermion type is found in skutterudites with Sr and Ba have lower Tc around 5.0 K.⁸⁻¹⁰

The formula of the ternary filled skutterudites, being derived from the mineral CoAs₃, is given by M₁TₓₜₓX₁₂, with M as a cation, T as a transition metal, and X as usually a pnictogen (P, As, or Sb).¹¹ The M atoms reside in large icosahedral cages formed by [TX₅] octahedra. A new family of superconducting skutterudites MPt₄Ge₁₂ (M=Sr, Ba, La, Pr, Th) has been reported recently.¹²⁻¹⁴ With trivalent La and Pt, Tc up to 8.3 K are observed. The compounds with the divalent cations Sr and Ba have lower Tc around 5.0 K.¹²,¹³

Band structure calculations predict that the electronic density of states (DOS) close to the Fermi level EF is determined by Ge 4p states in all MPt₄Ge₁₂ materials.¹²,¹³,¹⁵ The position of EF is adjusted by the electron count on the polyanionic host structure. This leads to the situation that the band structure at EF can be shifted in an almost rigid-band manner by “doping” of the polyanion, which can be achieved either by charge transfer from the guest M or by the internal substitution of the transition metal T. Recently, this principle was demonstrated on the Pt-by-Au substitution in BaPt₄Au₄Ge₁₆: while BaPt₄Ge₁₂ has a calculated DOS of 8.8 states/(eV f.u.), at the composition BaPt₄AuGe₁₂ the DOS is enhanced to 11.5 states/(eV f.u.).¹⁶ Experimentally, an increase in the superconducting Tc from 5.0 to 7.0 K (Ref. 16) was observed. The rigid-band shift of the DOS peak at EF with gold substitution is due to the Pt(Au) 5d electrons, which, according to band structure calculations, lie rather deep below EF and provide only a minor contribution to the DOS at EF.¹⁶

Another prediction from the band structure calculations concerns the special role played by the Pt 5d states in BaPt₄Ge₁₂ (SrPt₄Ge₁₂) for the chemical bonding. It is known, assuming two-center-two-electron bonds within the T-X framework for the binary skutterudites that 72 electrons are required for the stabilization of the [T₄X₁₂] formula unit.¹¹ In the case of SrPt₄Ge₁₂, the total number of s and p electrons of Sr, Pt, and Ge is 2+4×2+12×4=58. To achieve the target value of 72, each Pt atom should use 3.5d electrons for bonding, which would be a rather large value compared to the one d electron per Co atom in Co₃As₂ (4×CoAs₃).

In order to determine the electron counts for SrPt₄Ge₁₂ as a characteristic for the chemical bonding, we evaluated the so-called electron localizability indicator (ELI)¹⁷. The combination analysis of the ELI and electron density (ED) (see Fig. 1) shows indeed three types of attractors in the valence region: two representing Ge-Ge bonds and one reflecting the Pt-Ge bond. No attractors were found between Sr and the framework atoms, suggesting predominantly ionic interaction here. The Ge-Ge bonds are two-electron bonds (electron counts 1.90 and 2.01), the Pt-Ge bond has a count of only 1.53 electrons, summing up to 60.18 electrons total per [Pt₄Ge₁₂] formula unit. This means that only about 0.5 d electrons per Pt are participating in the stabilization of the [Pt₄Ge₁₂] polyanion. Both procedures, valence electron counting and combined ELI/ED analysis, yield unusual results and raise the question about the role of 5d electrons of Pt in the formation of the MPt₄Ge₁₂ compounds.

Up to now, no spectroscopic data are available to challenge the above-mentioned band structure predictions and chemical bonding analysis. Such a validation is important since one would like to know whether band theory can provide a solid basis for the modeling of superconductivity in
the MPt\textsubscript{4}Ge\textsubscript{12} ($M$ = Sr, Ba, La, Pr) series. We therefore set out to perform a comparative study of the valence-band electronic structure of the superconducting skutterudite derivative SrPt\textsubscript{4}Ge\textsubscript{12} by means of x-ray photoelectron spectroscopy (PES) and full-potential band structure calculations.

II. METHODS

Samples were prepared by standard techniques as described in Refs. 13 and 16. Metallographic and electron microprobe tests of polished specimens detected only traces of PtGe\textsubscript{2} (<4 vol %) and SrPt\textsubscript{2}Ge\textsubscript{2} (<1 vol %) as impurity phases in the sample SrPt\textsubscript{4}Ge\textsubscript{12}. Electron probe micro analysis (EPMA) confirmed the ideal composition of the target phase. The lattice parameter is 8.6509(5) Å, as reported previously.

For the cation position full occupancy was derived from full-profile crystal structure refinements of powder x-ray diffraction data, which are in good agreement with single-crystal data obtained in Ref. 12.

The PES experiments were performed at the Dragon beamline of the NSRRC in Taiwan using an ultrahigh-vacuum system (pressure in the low 10\textsuperscript{−10} mbar range) which is equipped with a Scienta SES-100 electron energy analyzer. The photon energy was set to 700 and 190 eV. The latter energy is close to the Cooper minimum in the photoionization cross section of the Pt\textit{5d} valence shell.\textsuperscript{18} The overall energy resolution was set to 0.35 eV and 0.25 eV, respectively, as determined from the Fermi cutoff in the valence band of a Au reference which was also taken as the zero of the binding-energy scale. The Fermi level is at zero energy.

FIG. 2 shows the calculated DOS for SrPt\textsubscript{4}Ge\textsubscript{12} ($E_F$ is at zero binding energy). The valence band is almost exclusively formed by Pt and Ge states. The low and featureless Sr DOS indicates that it plays basically the role of a charge reservoir. Further inspection of the DOS shows that the high-lying states between about 6 and 12 eV binding energies originate predominantly from Ge\textit{4s} electrons, whereas the lower-lying part of the valence band is formed by Pt\textit{5d} and Ge\textit{4p} states. The Pt\textit{5d} states essentially form a narrow band complex of approximately 3 eV bandwidth centered at about 4 eV binding energy. Our calculated DOS is in good agreement with the previous results of Bauer et al.\textsuperscript{12}

Figure 3 displays the valence-band photoemission spectra of SrPt\textsubscript{4}Ge\textsubscript{12} taken with a photon energy of $hv$=700 eV (upper panel) and 190 eV (middle panel), together with the reference spectrum of elemental Pt metal (bottom panel). The spectra are normalized to their integrated intensities after an integral background has been subtracted to account for inelastic scattering. All spectra show a clear cutoff at $E_F$ (zero binding energy) consistent with the systems being good metals. It is of no surprise that the 700 eV spectrum of SrPt\textsubscript{4}Ge\textsubscript{12} is very different from that of Pt since they are different materials. More interesting is that there are also differences between the 700 and 190 eV spectra of SrPt\textsubscript{4}Ge\textsubscript{12} itself. This is

![Graph](075114-2.png)

FIG. 2. (Color online) Calculated total and atom resolved partial electronic density of states of SrPt\textsubscript{4}Ge\textsubscript{12}. The Fermi level is at zero energy.

![Graph](075114-2.png)

FIG. 3. (Color online) Valence-band photoemission spectra of SrPt\textsubscript{4}Ge\textsubscript{12} taken with a photon energy of $hv$=700 eV (upper panel) and 190 eV (middle panel), together with the reference spectrum of elemental Pt metal (bottom panel). The spectra are normalized to their integrated intensities after an integral background has been subtracted to account for inelastic scattering. All spectra show a clear cutoff at $E_F$ (zero binding energy) consistent with the systems being good metals. It is of no surprise that the 700 eV spectrum of SrPt\textsubscript{4}Ge\textsubscript{12} is very different from that of Pt since they are different materials. More interesting is that there are also differences between the 700 and 190 eV spectra of SrPt\textsubscript{4}Ge\textsubscript{12} itself. This is
caused by differences in the photon energy dependence of the photoionization cross section of the relevant subshells forming the valence band, in this case, the Ge 4s, 4p, and Pt 5d. In fact, we chose those 190 and 700 eV photon energies in order to make optimal use of the cross-section effects for identifying the individual contributions of the Ge and Pt states to the valence band as we will show in the next sections. In particular, at 700 eV, the Pt 5d cross section is calculated to be a factor of 3.9 larger than that of the Ge 4p, while at 190 eV (close to the Cooper minimum for the Pt 5d) it is equal or even slightly smaller, i.e., a factor of 0.92 (see Table I). In other words, the 700 eV spectra are dominated by the Pt 5d contribution, while at 190 eV the contributions become comparable.

The intensity $I$ of a normalized spectrum as depicted in Fig. 3 is built up from the Pt 5d, Ge 4p, and Ge 4s partial DOS ($\rho$) weighted with their respective photoionization cross sections ($\sigma$). This is formulated in Eqs. (1) and (2) which take into account that the cross sections at 190 eV photon energy are different from those at 700 eV, respectively. The proportionality factors $c_{190}$ and $c_{700}$, respectively, also enter here since the absolute values for the photon flux and the transmission efficiency of the electron energy analyzer are not known. In addition, the constants $\alpha$, $\beta$, and $\gamma$ are introduced to express the nonuniqueness in the calculation of the weight of the Pt 5d, Ge 4p, and Ge 4s DOS, respectively, since these depend (somewhat) on which calculation method has been used,

\[ I_{700} = c_{190}[\sigma_{190}^{Pt 5d} / \sigma_{190}^{Ge 4p}] + c_{190}^{Ge 4s} / \sigma_{190}^{Ge 4s} + \sigma_{190}^{Ge 4s} \gamma / \sigma_{190}^{Ge 4s} + \sigma_{190}^{Ge 4s} \gamma / \sigma_{190}^{Ge 4s} \] \tag{1}

\[ I_{700} = c_{700}[\sigma_{700}^{Pt 5d} / \sigma_{700}^{Ge 4p}] + \sigma_{700}^{Ge 4s} / \sigma_{700}^{Ge 4s} + \sigma_{700}^{Ge 4s} \gamma / \sigma_{700}^{Ge 4s} + \sigma_{700}^{Ge 4s} \gamma / \sigma_{700}^{Ge 4s} \] \tag{2}

Using the predictions of the band structure calculations as a guide, we notice that the Ge 4s states hardly give a contribution in the energy range between the Fermi level and 6 eV binding energy. In this range, i.e., most relevant for the properties, the valence band seems to be determined mostly by the Pt 5d and Ge 4p states. We now analyze the experimental spectra along these lines. Using Eqs. (1) and (2), the Pt 5d and Ge 4p DOS can be experimentally extracted as follows:

\[ \rho^{Pt 5d} \sim I_{700} - A \times I_{190}, \] \tag{3}

\[ \rho^{Ge 4p} \sim I_{190} - B \times I_{700}, \] \tag{4}

with the parameters $A = (c_{700} / c_{190})(\sigma_{700}^{Ge 4p} / \sigma_{190}^{Ge 4p})$ and $B = (c_{190} / c_{700})(\sigma_{190}^{Pt 5d} / \sigma_{700}^{Pt 5d})$. While the cross sections $\sigma$ can be readily obtained from Table I, it would be an enormous task to determine (experimentally) the ratio between $c_{700}$ and $c_{190}$. Thus, since it is difficult to obtain directly an estimate for $A$ and $B$, we use the product $AB$ given by $(\sigma_{190}^{Pt 5d} / \sigma_{190}^{Ge 4p})/(\sigma_{700}^{Pt 5d} / \sigma_{700}^{Ge 4p})$, which can be calculated from Table I to be about 0.92/3.9=0.24. Therefore, we vary the values for $A$ and $B$ under the constraint that $AB=0.24$, searching for difference spectra which reproduce both the Pt 5d and the Ge 4p DOS as obtained by the band structure calculations.

We find good results for $A=0.6$ and $B=0.4$ as displayed in Figs. 4 and 5. Focusing first at Fig. 4 in which the rescaled 190 eV spectrum is subtracted from the 700 eV one, we can observe that the difference spectrum resembles very much that of the calculated Pt 5d DOS. Here, the latter has been broadened to account for the experimental resolution and lifetime effects. Interestingly, the main Pt intensity is positioned at around 3–6 eV binding energies and its weight near the $E_F$ region is very small. The experiment fully confirms this particular aspect of the theoretical prediction, which is important for the modeling of the superconducting properties as discussed above. We would like to note that the main peak of the calculated Pt 5d DOS is positioned at a somewhat lower binding energy than that of the experimental difference spectrum. Similar small deviations have been observed in other intermetallic materials and can be attributed to the inherent limitations of mean-field methods, such as the LDA, to calculate the dynamic response of a system.

### Table I. Calculated photoionization cross sections per electron ($\sigma$ in $\text{Mb/e}$) for the Pt 5d, Ge 4p and Ge 4s subshells, from Yeh and Lindau (Ref. 18).

<table>
<thead>
<tr>
<th>$h\nu$ (eV)</th>
<th>$\sigma^{Pt 5d}$</th>
<th>$\sigma^{Ge 4p}$</th>
<th>$\sigma^{Ge 4s}$</th>
<th>$\sigma^{Pt 5d} / \sigma^{Ge 4p}$</th>
<th>$\sigma^{Pt 5d} / \sigma^{Ge 4s}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>190</td>
<td>0.0099</td>
<td>0.0108</td>
<td>0.021</td>
<td>0.92</td>
<td>0.47</td>
</tr>
<tr>
<td>700</td>
<td>0.0074</td>
<td>0.0019</td>
<td>0.0030</td>
<td>3.9</td>
<td>2.5</td>
</tr>
</tbody>
</table>
Figure 5 shows the difference of the spectrum taken at 190 eV and the rescaled spectrum at 700 eV. This experimental difference spectrum reveals structures which can be divided into two major energy regions: the first region extends from 0 to 6 eV binding energy and the second from 6 to 12 eV. For the first region, we can make a comparison with the calculated Ge 4p DOS since the calculated Ge 4s contribution is negligible as explained above. We obtain a very satisfying agreement between the experiment and theory for the Ge 4p states. In particular, we would like to point out that the experiment confirms the strong presence of the Ge 4p states in the vicinity of the Fermi level $E_F$. Looking now at the second region (between 6 and 12 eV), we see that the calculated Ge 4s DOS also reproduces nicely the shape and the energy position of the experimental difference spectrum. Since the scaling parameters $A$ and $B$ for the intensity of the spectra have been determined between 0 and 6 eV binding energy, where the contribution of Ge 4s states is small, a better agreement of the Ge 4s related intensity between 6 and 12 eV binding energy cannot be expected. Here, we remark that the calculated Ge 4p DOS has a negligible contribution in this region.

As a further check, we also perform a comparison between the experimental photoemission spectrum of elemental Pt metal and the corresponding calculated Pt 5d DOS. The result is shown in Fig. 6. Also, here we find satisfying agreement between experiment and theory. The Pt 5d states range from 9 eV binding energy all the way up to $E_F$. Clearly, the high Fermi cutoff in Pt metal is formed by these Pt 5d states, in strong contrast to the SrPt$_4$Ge$_{12}$ case.

Figure 7 shows the Pt 4f core levels of SrPt$_4$Ge$_{12}$ (top) and elemental Pt metal (bottom). The spectra exhibit the characteristic spin-orbit splitting giving the $4f_{3/2}$ and $4f_{7/2}$ peaks. For SrPt$_4$Ge$_{12}$, the peak positions for the $4f_{3/2}$ and $4f_{7/2}$ are 75.4 and 72.1 eV binding energy, respectively. For Pt metal, the values are 74.4 and 71.1 eV, respectively. The spin-orbit splitting is thus 3.3 eV for both materials. This compares well with the calculated spin-orbit splitting of about 3.45 eV for both compounds from the LDA calculations.

Remarkable is that the SrPt$_4$Ge$_{12}$ 4f peaks are shifted by 1 eV to higher binding energies in comparison to those of Pt metal.
metal. Similar shifts have also been observed in other noble-metal intermetallic compounds, indicating a more dilute electron density around the noble-metal sites. To compare this chemical shift to LDA calculations, one has to take into account that the LDA does not incorporate many-body effects of the final state, manifesting in the asymmetric line shape of the spectra as discussed below in more detail. But it can be shown that final-state effects do not alter the average energy of the spectrum. If we determine the center of gravity of the $4f_{7/2}$, we find a binding energy of 72.4 eV for SrPt$_4$Ge$_{12}$ and 71.9 $\pm$ 0.2 eV (indicated by dashed lines in Fig. 7) for Pt metal, resulting in a chemical shift of 0.4 to 0.6 eV. This agrees well with the shift obtained from our band structure calculations which amounts to 0.43 eV.

One can clearly observe that the line shape of the core levels in SrPt$_4$Ge$_{12}$ is narrower and not as asymmetric as in the case of Pt metal. An asymmetry in the line shape is caused by the presence of electron-hole pair excitations upon the creation of the core hole, i.e., screening of the core hole by conduction-band electrons, and can be well understood in terms of the Doniach-Sunjic theory. The strong asymmetry of the $4f$ of Pt metal can therefore be taken as an indication for the high DOS with Pt 5d character at $E_F$. The rather symmetric line shape of the $4f$ of SrPt$_4$Ge$_{12}$, on the other hand, indicates very low DOS at $E_F$. All this confirms the results of the valence-band measurements: the main intensity of the Pt 5d band is at 3–6 eV binding energies, strongly reducing its weight at $E_F$.

IV. CONCLUSION

In conclusion, we find excellent agreement between the measured photoemission spectra and the LDA band structure calculations for SrPt$_4$Ge$_{12}$. This provides strong evidence that correlation effects beyond the LDA are of minor relevance in this compound. The excellent agreement confirms the picture of the chemical bonding analysis yielding rather deep lying Pt 5d states which only partially form covalent bands with the Ge 4p electrons. In turn, the states at the Fermi level that are relevant for the superconducting behavior of this compound can be firmly assigned to originate predominantly from Ge 4p electrons. This study provides strong support that the band theory is a good starting point for the understanding of the electronic structure of the MPt$_4$Ge$_{12}$ ($M=$Sr, Ba, La, Pr, Th) material class and is thus of valuable help in the search for new compositions with higher superconducting transition temperatures.

11The parameter $y$ in $M_yT_{x_2}$ ($y \leq 1$) indicates the (likely intrinsic) incomplete filling of the $M$ site for several compounds in the family.
22M. Kohout, BASIN, version 4.7 (2008).