Giant Overlap between the Magnetic and Superconducting Phases of CeAu$_2$Si$_2$ under Pressure

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High pressure provides a powerful means for exploring unconventional superconductivity which appears mostly on the border of magnetism. Here, we report the discovery of pressure-induced heavy-fermion superconductivity up to 2.5 K in the antiferromagnet CeAu$_2$Si$_2$ ($T_N \approx 10$ K). Remarkably, the magnetic and superconducting phases are found to overlap across an unprecedentedly wide pressure interval from 11.8 to 22.3 GPa. Moreover, both the bulk $T_c$ and $T_N$ are strongly enhanced when increasing the pressure from 16.7 to 20.2 GPa. $T_c$ reaches a maximum at a pressure slightly below $p_c \approx 22.5$ GPa, at which magnetic order disappears. Furthermore, the scaling behavior of the resistivity provides evidence for a continuous delocalization of the Ce 4f electrons associated with a critical end point lying just above $p_c$. We show that the maximum $T_c$ of CeAu$_2$Si$_2$ actually occurs at almost the same unit-cell volume as that of CeCu$_2$Si$_2$ and CeCu$_2$Ge$_2$, and when the Kondo and crystal-field splitting energies become comparable. Dynamical mean-filed theory calculations suggest that the peculiar behavior in pressurized CeAu$_2$Si$_2$ might be related to its Ce-$4f$ orbital occupancy. Our results not only provide a unique example of the interplay between superconductivity and magnetism, but also underline the role of orbital physics in understanding Ce-based heavy-fermion systems.

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1. INTRODUCTION

Superconductivity (SC) and magnetism were long thought to be antagonistic. In this context, the discovery 22 years ago that high pressure turns a magnetically ordered heavy-fermion (HF) compound, namely, CeCu$_2$Ge$_2$, into a superconductor has attracted much attention in the condensed matter physics community [1]. Since then, high-pressure studies of Ce-based HFs have revealed a number of superconductors such as CePd$_2$Si$_2$ [2], CeIn$_3$ [3], CeRhIn$_5$ [4], and, more recently, CePt$_2$In$_7$ [5]. In all known cases, SC emerges in the vicinity of a magnetic-nonmagnetic phase boundary, and most often competes for stability with magnetic order, except in a few examples where both states coexist within a narrow pressure range [6].

CeCu$_2$Ge$_2$ is an isostructural sister compound of the first discovered HF superconductor CeCu$_2$Si$_2$ [7], which exhibits a second superconducting phase under pressure with a higher $T_c$ [8–12]. Remarkably, CeCu$_2$Ge$_2$ shares the same phase diagram as CeCu$_2$Si$_2$ when pressurized above $\sim 10$ GPa, where magnetism disappears [9,13]. Indeed, both compounds feature the existence of connected low- and high-pressure superconducting phases associated with two critical points of different origins. Moreover, the partial substitution of Si by Ge in CeCu$_2$Si$_2$ results in the splitting of the initially joined superconducting phases into two distinct domes due to disorder-induced pair breaking [14].

Despite three decades of efforts, the underlying mechanisms for the two superconducting phases are still poorly understood. On one hand, it is widely believed that SC at low pressure is mediated in these systems by critical spin fluctuations [15,16]. However, this view was very recently challenged by a thermodynamical study that points to multiband SC with a full energy gap in CeCu$_2$Si$_2$ at ambient pressure [17]. On the other hand, there is no general consensus that critical valence fluctuations are responsible for high-pressure SC [10,18]. An alternative interpretation is that critical fluctuations stemming from orbital transition provide the glue of the superconducting pairing [19,20].
In this regard, exploration of high-pressure SC in close relatives of CeCu$_2$Si$_2$ is highly desirable. For such investigation, the isoelectronic and isostructural compound CeAu$_2$Si$_2$ is an excellent candidate. At ambient pressure, CeAu$_2$Si$_2$ orders antiferromagnetically below $T_N \approx 10$ K. A previous high-pressure study of a polycrystalline sample, carried out down to 1.2 K, shows that while the magnetic order disappears around 16 GPa, SC does not occur below 19.5 GPa [21].

In this paper, we report on pressure-induced SC in high-quality CeAu$_2$Si$_2$ single crystals with $T_c$ reaching 2.5 K observed from high-pressure “multiprobe” (transport and calorimetry) measurements up to 27.4 GPa. Unexpectedly, the resulting pressure-temperature phase diagram reveals a highly unusual interplay of superconductivity with magnetism, and differs markedly from that of all known Ce-based pressure-induced superconductors. In particular, for the first time, both superconductivity and magnetism are enhanced with increasing pressure over a broad pressure region. We present a comparison of the unit-cell volume phase diagram of CeAu$_2$Si$_2$ with that of CeCu$_2$Si$_2$ and CeCu$_2$Ge$_2$ and discuss the implication of these results on the pairing mechanism. First-principles calculations show the existence of an intermediate state in the pressure dependence of the Ce-4$f$ orbital occupancy for CeAu$_2$Si$_2$, which may be a key ingredient for understanding the peculiar behavior in this compound.

II. METHODS

We grow single crystals of CeAu$_2$Si$_2$ by the “flux” method (see Ref. [22] for guidelines) using Au-Si self-flux and Sn flux. The starting materials are Ce (99.99%) from Ames Lab [23], Au (99.999%), Si (99.9999%), and Sn (99.9999%) from Alfa-Aesar. In the self-flux method, elements with a ratio of Ce$_{0.05}$Au$_{0.475}$Si$_{0.475}$ are melted in an alumina crucible inside a sealed evacuated quartz ampoule, held at 1120 °C for 6 h, followed by a slow cooling at 1.2 °C/h down to 850 °C. In the Sn-flux method, which is slightly different from that described in Ref. [24], an ingot of Ce: Au: Si = 1:20:3 is presynthesized by arc melting under an argon atmosphere and flipped five times to ensure homogeneity. Big pieces of the crushed ingot are melted with Sn (CeAu$_{20}$Si$_3$: Sn = 1:50) in an alumina crucible inside a sealed evacuated quartz ampoule, held at 1150 °C for 48 h, followed by a slow cooling at 1 °C/h down to 650 °C. In both cases, crystals, separated from the flux by centrifugation, exhibit well-developed facets and have sizes of up to a few centimeters. Phase impurities are not detected by XRD nor by SEM-EDX measurements. The ambient-pressure measurements show that, within the uncertainty of the geometrical factor, the difference between the Sn-flux and the self-flux samples’ resistivity values is almost temperature independent, and their respective residual resistivities are 1.8 and 12.2 $\mu$Ω cm.

High-pressure experiments are performed in a Bridgman-type sintered diamond anvil pressure cell using steatite as the pressure-transmitting medium and lead (Pb) as the pressure gauge [25]. A photograph of the actual setup is shown in Fig. S1 of the Supplemental Material [26]. The CeAu$_2$Si$_2$ sample, arranged in such a way that the $c$ axis is parallel to the compressive force, is connected in series with the Pb for four-probe resistivity measurements. The ac-calorimetry measurements and data analysis are carried out according to the method described in Ref. [27]. The chromel wire, which otherwise serves as one of the voltage leads, is used as the heater and is thermally excited by an ac current of frequency $\omega$ while the sample temperature oscillations are detected by measuring the voltage of the Au/AuFe thermocouple $V_{ac}$ at a frequency of $2\omega$. The data recorded at frequencies above and well below the cutoff frequency correspond, respectively, to a signal dominated by the sample contribution, which can be considered to be inversely proportional to the heat capacity, and to a measure of the mean elevation of the sample temperature over that of the bath. Note that the resistance of the chromel wire is almost pressure independent and more than 2 orders of magnitude larger than that of the sample. Hence, the possibility that the observed anomalies are due to the drastic change in heating power can be ruled out. Throughout the experiments, the pressure gradient estimated from the width of the Pb superconducting transition is $\Delta p \leq 0.3$ GPa. After depressurization, examination of the pressure chamber shows that the distance between the voltage leads has increased by less than 10%. This, together with the geometrical factor uncertainty as well as the change in the sample volume under pressures, sets a 15% error on the absolute resistivity value.

Theoretical calculations are performed based on a combination of electronic structure and dynamical mean-field theory (DMFT) methods, which takes into account both the local atomic physics and correlation effects in the Ce $f$ shell as well as the physical effects of hybridization with conduction electrons [renormalization of crystal-field (CF) levels and Kondo screening] [20]. Our self-consistent (over the charge density) implementation of this method is that of Refs. [28,29] and uses the full-potential linear-augmented plane-wave electronic structure Wien2k [30] code. The DMFT quantum impurity problem is solved with the continuous-time quantum Monte Carlo (CTQMC) method [31] based on the TRIQS library [32] package.

The Wannier orbitals representing Ce-4$f$ states are constructed from the Kohn-Sham states within the energy range from $-12.4$ to $5.4$ eV using the projective approach of Ref. [28]. The local Coulomb interaction between Ce-4$f$ electrons is approximated by a spherically symmetric density-density form parametrized by the Slater parameter $F_0 = U = 6.36$ eV [33] and Hund’s rule coupling $J = 0.7$ eV used previously in Ref. [20]. The fully-localized-limit form of the double-counting correction term is employed throughout.
We use the eigenstates $|\Gamma\rangle$ of Ce$^{3+}$, obtained by diagonalizing the ab initio crystal-field and spin-orbit Hamiltonian, as a basis for CTQMC calculations. Rather small off-diagonal elements of the DMFT hybridization function in the $\{\Gamma\}$ basis are neglected. This approximation allows us to treat the full Ce-4$f$ shell and to access low temperatures using the fast “segment picture” algorithm of the CTQMC method [31]. The DMFT quantum impurity problem is solved using up to $4 \times 10^{11}$ CTQMC moves with a measurement performed after each 200 moves. The calculations are performed for the body-centered tetragonal ThCr$_2$Si$_2$-type structure at the experimental value of the lattice parameters determined as a function of pressure in Refs. [34–36].

III. RESULTS AND DISCUSSION

A. Experimental results of CeAu$_2$Si$_2$

The general trend of the electrical resistivity of the investigated CeAu$_2$Si$_2$ single crystals as a function of pressure ($p$) and temperature ($T$) (see Fig. S2 of the Supplemental Material [26]) is typical of Ce-based Kondo lattice systems [9]. However, our samples show a 30 times lower residual resistivity ($\rho \approx 1.8 \mu\Omega\text{cm}$ at $p = 0$) than reported previously [21]. The temperature dependence of the magnetic contribution $\rho_{\text{mag}}$ to resistivity at representative pressures, shown in Fig. 1(a), is obtained by subtracting the phonon contribution approximated as a pressure-independent term $\rho_{\text{ph}} \approx 0.0627 (\mu\Omega\text{cm})$ [37] from the raw data. Below room temperature, the ambient-pressure curve already unveils two anomalies of weak magnitude. One can discern a maximum at $\sim 140$ K, as well as the onset of a low-temperature anomaly, which is masked by the sharp drop in resistivity ascribed to the magnetic ordering below $T_N \approx 10$ K. At an intermediate pressure of 14.2 GPa, these anomalies have grown markedly and $\rho_{\text{mag}}(T)$ exhibits two characteristic maxima at temperatures $T_{\text{max}}^1 \approx 8$ K and $T_{\text{max}}^2 \approx 137$ K. Above each of these maxima, $\rho_{\text{mag}}(T)$ follows specific $-\ln T$ dependencies, which reflect the incoherent Kondo scattering of the ground state and excited crystal-field levels, respectively [38]. When increasing pressure up to 20.2 GPa, the Kondo scattering keeps increasing. The temperature $T_{\text{max}}^2$ remains almost unchanged, while $T_{\text{max}}^1$ has by now started its rise. At the highest measured pressure of 27.4 GPa, the two maxima have already merged. The contribution at $T_{\text{max}}^1$ dominates in such a way that a single peak is observed at $\sim 200$ K. Connected to this behavior, the $-\ln T$ resistivity slope becomes steeper with increasing pressure, which is interpreted as resulting from a dramatic rise in Kondo temperature ($T_K$) of $2 \frac{1}{2}$ orders of magnitude over the investigated pressure range [38].

For the first time, signatures of both superconducting and magnetic transitions are observed in resistivity and heat capacity measurements of CeAu$_2$Si$_2$, as exemplified in Fig. 1(b) (see also Fig. S3 of the Supplemental Material [26]). It can be seen that at 20.2 GPa, the resistive superconducting transition around 2.2 K coincides with a jump ($\sim 20\%$ of the total signal) in $C^\text{ac}(T)$, indicating bulk SC. Such an anomaly due to SC is detected at pressures as high as 24.5 GPa. By contrast, at 15.9 GPa, despite the sharp and complete resistive transition, no corresponding anomaly is detected in $C^\text{ac}(T)$, indicating that SC is likely filamentary or textured [39]. It is worth noting that at 15.9 and 20.2 GPa, the jump in heat capacity together with the downward change of slope in resistivity (distinctively above $T_c$) are evidence of the persistence of a magnetic ordering, presumably of antiferromagnetic nature. In line with common practice [40], the superconducting and magnetic-ordering temperatures $T_c$ and $T_M$ in $C^\text{ac}(T)$ are defined by the midpoint of the respective jumps when considering entropy conservation. As an example, the two up-down arrows show that at 20.2 GPa the two midpoints agree well with the completeness of the resistive transition ($T_c^2 \approx 2.2$ K) and the onset of downward curvature in the resistivity ($T_M \sim 4.5$ K), respectively.

The pressure dependencies of both $T_M$ and $T_c$ define the phase diagram shown in Fig. 2(a), which reveals several remarkable new features. Even though the magnetism persists up to $\sim 22$ GPa, SC is found over the very broad

FIG. 1. (a) Logarithmic temperature dependence of the magnetic contribution $\rho_{\text{mag}}$ to the in-plane resistivity of CeAu$_2$Si$_2$ for typical pressures. The two characteristic maxima $T_{\text{max}}^1$ and $T_{\text{max}}^2$ at 14.2 GPa are marked by the arrows. The dotted red lines are a guide to the eyes, showing the $-\ln T$ dependence of the resistivity. Note that with increasing pressure, $T_{\text{max}}^1$ increases drastically while $T_{\text{max}}^2$ remains almost constant, and finally the two maxima merge into a single peak. (b) Comparison of the resistivity $\rho$ and heat capacity $C^\text{ac}$ (in arbitrary unit) for three different pressures at which complete resistive superconducting transitions were observed. A jump in $C^\text{ac}$ due to SC coincides with the completeness of the resistive transition at 20.2 and 24.5 GPa, but is absent at 15.9 GPa. At 15.9 and 20.2 GPa, the jump in $C^\text{ac}$ above $T_c$ accompanied by a change in the slope of $\rho$ indicates the magnetic ordering. As an example, two arrows show that at 20.2 GPa the jumps in $C^\text{ac}$ correspond well to the magnetic transition ($T_M \sim 4.5$ K) and to the completeness of the resistive transition ($T_c^2 \approx 2.2$ K).
higher pressures, coupling, in agreement with previous data [21], but at
marks the anomalies in the measurements). The data from Ref. [21] are also included for
(closed) symbols denote the data extracted from only the pressure range 11.8
The inset shows the collapse of all normalized data
dependence, whose anomalies are clearly connected to SC. Indeed, the emergence of filamentary and bulk SC each correspond to a strengthening of magnetism, which manifests itself in the $T_M$ evolution by a flattening and a cusp, respectively. These anomalies may signal the formation of new magnetic phases [41]. In the pressure interval 11.8–15.9 GPa, where $T_c$ onset increases while $T_M$ decreases, SC appears to compete with magnetism as usually observed [6]. However, at higher pressures up to 20.2 GPa, there is a dramatic rise of the $T_M$ from ~2.5 to ~4.5 K. Remarkably, this rise corresponds to a reduction of the heat capacity anomaly. Moreover, in the same pressure range, the bulk $T_c$ also increases strongly (by a similar factor) from ~1.4 to ~2.3 K while the width of the resistive transition remains narrow ($\Delta T_c < 0.3$ K). Consequently, it is unlikely that SC and magnetic order originate from separated phases. Such a simultaneous enhancement of both $T_M$ and $T_c$ over a broad pressure range has never been reported in any other Ce-based pressure-induced superconductors.

With increasing pressure above 21.6 GPa, the signature of magnetic ordering is present only in resistivity, and $T_M$ (see Fig. S4 of the Supplemental Material [26] for its determination) decreases rapidly and drops to zero between 22.3 and 22.8 GPa, indicating a magnetic quantum critical point (QCP) at $p_c = 22.5 \pm 0.3$ GPa. Correspondingly, the fitting of the power law $\rho(T) = \rho_0 + AT^n$ to the resistivity data above $T_c$, where $\rho_0$ is the residual resistivity, yields a maximum $A$ coefficient and a minimum exponent ($n \approx 1.5$) at $p_c$, both of which are standard signatures of a QCP [see Fig. 2(a), inset]. Note that the uncertainty in $p_c$ is comparable to the pressure gradient inside the pressure chamber, and thus, the phase transition could be weakly first order, which raises questions about the quantum nature of $p_c$. On the other hand, at pressures below 22 GPa, the power-law analysis is not pertinent due to the strong magnetic contribution to the resistivity below $T_M$. In order to highlight the ground-state excitations independently of magnetic ordering, we plot the isothermal resistivity at 5 K, i.e., just above $T_M$ for $p > 7$ GPa, versus pressure, as shown in Fig. 2(b). Clearly, the resistivity at 5 K shows a broad peak of high magnitude at around 17 GPa, which roughly coincides with the local minimum in $T_M$ and the onset of bulk SC. This observation supports the existence of a putative QCP around the pressure at which the maximum scattering rate occurs. At $p_c$, only a weak anomaly is seen whose magnitude is smaller than the term $AT^{1.5}$ (with $T = 5$ K), as expected.

Slightly below $p_c$, $T_c$ reaches a maximum of ~2.5 K, which is among the highest values reported to date for Ce-based HF superconductors. In order to further characterize the superconducting state, we measure the resistive transition at 22.3 GPa under various magnetic fields ($B$) applied along the crystal’s c axis (see Fig. S5 of the Supplemental Material [26]). The results show a very large initial slope of the upper critical field $\frac{dB_{c2}}{dT}$ at $T_c = -7.1$ T/K, and given that $\frac{dB_{c2}}{dT}|_{T_c} \propto m^2 T_c$ [42], a very large effective mass $m^* \sim 110 m_0$ ($m_0$ is the free-electron mass) is

FIG. 2. (a) Experimental $\rho$–$T$ phase diagram of CeAu$_2$Si$_2$. $T_{onset}$ and $T_M$ represent the superconducting transition onset and the magnetic ordering temperatures, respectively. The open (closed) symbols denote the data extracted from only the resistivity measurements (from both resistivity and heat capacity measurements). The data from Ref. [21] are also included for comparison, and a good agreement is found. The two arrows mark the anomalies in the $T_M(p)$ curve at ~11 and ~16 GPa, in accordance with the emergence of filamentary and bulk SC. The inset shows the fitting parameters of the power law $\rho(T) = \rho_0 + AT^n$ to the resistivity data above $T_c$, plotted as a function of pressure. The $A$ coefficient reaches a maximum and the temperature exponent $n$ exhibits a minimum at $p_c \approx 22.5$ GPa, where the magnetic order disappears. (b) Plot of $\rho$ versus $p$ at 5 K. The data exhibit one peak at ~17 GPa (onset of bulk SC) and a shoulder at ~$p_c$. (c) Plot of $\rho^* = \rho - \rho_0$ versus $p$ at selected temperatures up to 30 K. The solid black circles indicate the 50% drop of $\rho^*$ compared to its value at 22.8 GPa for each isotherm. The inset shows the collapse of all normalized data $\rho_{\text{norm}}$ when plotted against the generalized distance $h/\theta$ from the critical end point located at $p^* \approx 23.6$ GPa and $T_{\text{onset}} = 14$ K (see text for details). The two critical pressures $p_c$ and $p^*$ are indicated by labeled arrows.

pressure range 11.8–26.5 GPa, resulting in a giant overlap of the two phases. At low pressure, $T_M$ first displays a linear-in-$T$ decrease due to the increase of the Kondo coupling, in agreement with previous data [21], but at higher pressures, $T_M$ shows an atypical nonmonotonic dependence, whose anomalies are clearly connected to
obtained, confirming heavy-fermion SC. Furthermore, using the extrapolated upper critical field at zero temperature \(B_c(0) \sim 9.2\, \text{T}\), the Ginzburg-Landau (GL) coherence length \(\xi_{GL}\) is estimated as \(\xi_{GL} = \sqrt{\Phi_0/2\pi B_c(0)} \approx 55\, \text{Å}\), where \(\Phi_0\) is the flux quantum. Preliminary measurements show that \((dB_c/dT)_T\) scales with \(T_c\).

Just above the pressure \(p_{cr}\), in parallel with the decrease of \(T_c\), the low-temperature isothermal resistivity \(\rho'(p) = \rho(p) - \rho_0(p)\) goes down steeply with increasing pressure, as shown in Fig. 2(c). This behavior is reminiscent of what is found in the vicinity of the second critical point of CeCu$_2$Si$_2$ around 4.5 GPa, a behavior that is analyzed assuming an underlying critical end point located at \((p_{cr}, T_{cr})\) in the \(p-T\) plane [12]. Following the same data treatment, we define the normalized resistivity \(\rho_{norm}(p) = [\rho'(p) - \rho'(p_{50\%})]/\rho'(p_{50\%})\), where for each temperature, \(p_{50\%}\) denotes the pressure corresponding to the midpoint of the \(\rho'(p)\) drop compared to its value at 22.8 GPa. As shown in the inset of Fig. 2(b), the \(\rho_{norm}\) data below 30 K collapse onto a single curve, when plotted as a function of \(h/\theta\), where \(h = (p - p_{50\%})/p_{50\%}\) and \(\theta = (T - T_{cr})/|T_{cr}|\) with the only free parameter \(T_{cr} = -14\, (2)\, \text{K}\). Such a scaling shows that the resistivity is fully governed by the proximity of a critical end point in a broad region of the \(p-T\) plane \((p > p_{cr}, T \leq 30\, \text{K})\). Moreover, the slightly negative \(T_{cr}\) value substantiates that CeAu$_2$Si$_2$ just misses a first-order transition, meaning that only a crossover occurs. By extrapolating the temperature dependence of \(p_{50\%}\) to zero temperature, we obtain \(\rho'(p_{cr}) = 23.6 \pm 0.5\, \text{GPa}\).

To check the reproducibility of the above results, we perform measurements on CeAu$_2$Si$_2$ crystals, grown by a self-flux (Au-Si) method (unpublished results). Although the residual resistivity \(\rho_0\) of these crystals is about 5 times higher than that of the present study, the pressures \(p_{cr}\) and \(p'\) are found to be almost identical to the aforementioned values, clearly indicating that they are intrinsic and not affected by the sample quality. Around \(p'\), a scaling of resistivity is also obtained with a slightly more negative \(T_{cr}\). Moreover, we observe a similar resurgence of magnetism for \(p > 15\, \text{GPa}\). However, for the self-flux grown crystals, SC emerges only from 20 GPa and the maximum \(T_c \sim 1.1\, \text{K}\) is considerably lower. We attribute this to a strong pair-breaking effect, especially in the magnetic phase, when the electron mean free path \(\ell' \propto 1/\rho_0\) is short, consistent with observations in CeCu$_2$Ge$_2$ [9]. This also explains why no SC was detected at all in the previous study, which was performed on polycrystalline samples with an even higher \(\rho_0\) value [21].

**B. Comparison with CeCu$_2$Si$_2$ and CeCu$_2$Ge$_2**

In order to allow for a straightforward comparison of CeAu$_2$Si$_2$ and CeCu$_2$X$_2$ \((X = \text{Si or Ge})\), we convert the pressure into the unit-cell volume \((V)\) of each compound, using high-pressure crystallographic results [34–36] (see the caption of Fig. 3). The three corresponding \(V-T\) phase diagrams are shown in Fig. 3. Strikingly, despite the very different properties observed at ambient pressure (notably the ambient pressure volume \(V_0\)), there is a broad overlap of the bulk superconducting regions of the three compounds, which confirms that the local environment of the Ce ions plays a key role in the occurrence of SC. In particular, the \(V\) dependencies of \(T_c\) are nearly identical for CeCu$_2$X$_2$, and their maximum \(T_c\)'s occur at the same \(V' \approx 158\, \text{Å}^3\), far away from the volume at which magnetism disappears in CeCu$_2$Ge$_2$ and in good agreement with a previous report [43]. This excellent match resembles the one obtained for the magnetic phase diagrams of CePd$_2$Si$_2$ and CePd$_2$Ge$_2$, when plotted versus their \(V\) [44].
For CeAu$_2$Si$_2$, the maximum $T_c$ is slightly shifted to a larger $V$. This shift of about 2 Å$^3$ seems beyond experimental error and might indicate the limit of our comparison in terms of the unit-cell volume. Since we compare isostructural and isoelectronic compounds, the unit-cell volume is certainly a relevant parameter, although it is not ideal. For instance, when pressure reduces the $V$ of CeAu$_2$Si$_2$ to that of CeCu$_2$Si$_2$, the Au and Cu atoms may still contribute differently to the crystal-field effect.

The phase diagram of CeAu$_2$Si$_2$ exhibits two qualitative differences with that of CeCu$_2$X$_2$. First, SC emerges deep inside the magnetic region. Second, magnetic ordering persists down to a smaller $V$, and its disappearance coincides with the maximum $T_c$. This latter characteristic, which is the most common case for Ce-based pressure-induced superconductors, can be taken as strong evidence that SC in CeAu$_2$Si$_2$ is mediated by critical spin fluctuations [6]. The fact that the onsets of filamentary and bulk SCs correlate with the anomalies in the $T_M$ evolution [see also Fig. 2(a)], hinting at the existence of two putative QCPs, points to a deep link between SC and magnetic instabilities. However, the simultaneous enhancement of both SC and magnetic order in a wide volume (pressure) range, which has never been seen in any other Ce-based pressure-induced superconductors, can hardly be explained by this scenario. Instead, it is plausible that SC and magnetic order are not intrinsically related phenomena, although the possibility that SC develops from the magnetic-ordered state cannot be excluded. This is further corroborated by the comparison of CeAu$_2$Si$_2$ and CeCu$_2$X$_2$, made in Fig. 3, which shows that a similar maximum $T_c$ occurs regardless of the presence or the absence of a magnetic QCP. Thus, it appears that another pairing mechanism is involved at least on the low-volume side of the superconducting region.

Another interesting clue pointing in this last direction is found in Fig. 3: for all three compounds, the maximum $T_c$ occurs when the temperatures $T_{1 \text{max}}^\text{max}$ and $T_{2 \text{max}}^\text{max}$ of the resistivity maxima [as defined in Fig. 1(a)] merge, at relatively high temperature (~40$T_c^{\text{max}}$). Notice that in CeAu$_2$Si$_2$, $T_{1 \text{max}}^\text{max}$ joins $T_{2 \text{max}}^\text{max}$ at a slightly larger $V$ than that for CeCu$_2$X$_2$, similar to the small $V$ shift observed for the $T_c$ maximum. Since the three quantities are measured at each pressure run, their correspondence is unaffected by the uncertainty of pressure determination and hence significant. Although the exact relationships are yet to be determined, it is empirically known that the temperatures $T_{1 \text{max}}$ and $T_{2 \text{max}}$ scale approximately with the Kondo temperature ($T_K$) and CF splitting energy, respectively [45]. In our case, $T_{1 \text{max}}^\text{max}$ gives an indication of $T_K$ only for $V < 165$ Å$^3$ (i.e., $T_{1 \text{max}}^\text{max} > 10$ K) when the low-temperature resistivity maximum is free from the influence of magnetic ordering. As can be seen in Fig. 3, for $V < 165$ Å$^3$, $T_{1 \text{max}}^\text{max}$ ($\propto T_K$) shows a nearly exponential increase with decreasing $V$ and appears as the driving parameter of the system, which makes it evolve from long-range magnetic-ordered states, through SC, towards a strongly delocalized paramagnetic $f$ metal at reduced volume. Therefore, we conclude that the superconducting pairing is strongest when Kondo and CF splitting energy scales become comparable. Moreover, $T_{1 \text{max}}^\text{max}$ governs the ground-state excitations reflected by the low-temperature resistivity in the paramagnetic phase. For CeCu$_2$X$_2$, the relationship $T_{1 \text{max}}^\text{max} \propto 1/\sqrt{A}$ (where $A$ is the Fermi liquid resistivity coefficient) is shown to be fulfilled, except around $p^*$, where $A$ abruptly drops by 1 order of magnitude [10]. Hence, above $p_c$, the $A$ values of CeAu$_2$Si$_2$ [see inset of Fig. 2(a)] are similar to those of CeCu$_2$X$_2$ taken at the same $V$. Finally, we note that in comparison with CeCu$_2$X$_2$, $T_{2 \text{max}}^\text{max}$ of CeAu$_2$Si$_2$ is almost 2 times higher, and $T_{1 \text{max}}^\text{max}$ shows a slower rise for $V$ just below 165 Å$^3$, which could account for the persistence of magnetism according to Doniach’s simple scheme [46]. In passing, we remark that for CePd$_2$Si$_2$, SC also occurs when both Kondo resistivity and crystal-field contribution peaks merge [44,47]. It can be conjectured that this feature is a generic property of Ce-based HF superconductors.

In previous publications, the high-pressure superconducting dome of CeCu$_2$X$_2$ was interpreted within the framework of the critical valence fluctuation theory [10,48,49]. According to this approach, the critical end point of the valence transition line of the Ce ion lies at a pressure $p_c$ and a temperature $T_{cr}$ close to 0 K. This theory provides a consistent interpretation of most of the features observed in the vicinity of $p_c$, which include, besides SC, a collapse of the resistivity associated with a $T$-linear regime, an enhanced residual resistivity, and the above-mentioned merging of the two temperatures $T_{1 \text{max}}$ and $T_{2 \text{max}}$ [10,11,49]. However, around $p_c$, calculations predict a strong decrease of the Ce-4$f$ orbital occupancy with increasing $p$, while x-ray absorption measurements show a considerably smaller variation (by a factor of 5) [18]. This disagreement and the clue that at the maximum $T_c$ the energy scale of the system is of the order of the CF splitting energy drew us to examine the role played by the orbital states and the associated fluctuations of the Ce-4$f$ electrons in the properties of these materials [19,20].

C. Comparison to dynamical mean-field theory calculations

As a first step to address this issue, we perform calculations based on a combination of electronic structure and DMFT [50] methods, along similar lines as in Ref. [20] for CeCu$_2$Si$_2$. In a tetragonal crystal field, the $^2F_{5/2}$ ground-state multiplet of the Ce$^{3+}$ ion is split into three doublets: $|0\rangle = a|\pm 5/2\rangle + \sqrt{1-a^2}|\mp 3/2\rangle$, $|1\rangle = |\pm 1/2\rangle$, and $|2\rangle = \sqrt{1-a^2}|\pm 5/2\rangle - a|\mp 3/2\rangle$. A key difference between CeAu$_2$Si$_2$ and CeCu$_2$Ge$_2$ is already apparent from our results calculated at ambient pressure and lowest pertinent temperature (7 K). While for both compounds
the ground state is associated with state $|0\rangle$, the first excited state is $|1\rangle$ in CeAu$_2$Si$_2$ but $|2\rangle$ in CeCu$_2$Ge$_2$. In order to fully take into account the hybridization and Kondo effects, this splitting can be obtained from the location of the respective Kondo peaks in the orbitally resolved spectral functions. For CeAu$_2$Si$_2$, we obtain levels $|1\rangle$ and $|2\rangle$ to be, respectively, 9.8 and 24.5 meV above the main Kondo peak associated with state $|0\rangle$, in reasonable agreement with the reported experimental values of 17 and 21 meV [51]. By contrast, for CeCu$_2$Ge$_2$, we find these splitting to be 34 and 19 meV, respectively. Note that for CeCu$_2$Ge$_2$, the ambient-pressure ground state has been experimentally ascribed to state $|2\rangle$, although this identification is based on simulations of the temperature dependence of the uniform magnetic susceptibility with the CF levels treated as quasistatic levels neglecting hybridization and Kondo effects [52].

Correspondingly, another key difference between CeCu$_2$Ge$_2$ and CeAu$_2$Si$_2$ is that the occupation of state $|1\rangle$ at ambient pressure is very small for the former while it is sizable for the latter, as displayed on Fig. 4 (upper panels). In this figure, we plot the evolution of the occupancies of each state as a function of pressure for the two compounds. For CeCu$_2$Ge$_2$, the occupancy of state $|1\rangle$ remains negligible at all pressures, but a transition between a regime dominated by state $|0\rangle$ at low pressure and a regime dominated by state $|2\rangle$ at high pressure takes place, with the occupancy of the two levels crossing each other around 17 GPa. Across the transition region, the $f$ electron weight is transferred from the CF state $|0\rangle$ to the excited level $|2\rangle$, due to the latter’s stronger hybridization with itinerant electrons. This “orbital transition” is quite similar to the one recently discussed theoretically [19,20] for CeCu$_2$Si$_2$, except that it is shifted to higher pressure by about 15 GPa in the Ge-based compound. In contrast, the pressure evolution in the upper panel of Fig. 4 clearly displays three distinct regimes: one dominated by state $|0\rangle$ at low pressure (roughly below 10 GPa), one dominated by state $|2\rangle$ at high pressure ($\gtrsim$20 GPa), and an additional intermediate regime (roughly between 10 and 20 GPa) where all three states contribute. We have also followed the evolution of these three regimes as a function of temperature, and the result is visualized in Figs. 4(c) and 4(d) as a color map in the $(p, T)$ plane.

Although our calculations are not performed in the phase with magnetic long-range order, our results do hint at a qualitatively different behavior of the two compounds, as observed experimentally. It is tempting, in particular, to relate the three different regimes found for CeAu$_2$Si$_2$ to the observed persistence and revival of magnetism in the 15–20 GPa range, and possibly to the existence of several different magnetic phases (as suggested by the kinks and nonmonotonic behavior of the magnetic transition temperature $T_m$ versus pressure). In contrast, in CeCu$_2$Ge$_2$, one observes a single magnetic phase that collapses at a significantly lower pressure than the maximum of the SC dome. Moreover, the pressure evolution of the Kondo temperature $T_K$ ($\propto T_1^{\text{max}}$) in CeAu$_2$Si$_2$ (Fig. 3) is different than in CeCu$_2$Ge$_2$, with an intermediate slower increase in the range 10–16 GPa. Indeed, this is consistent with our calculated evolution of the effective mass, which displays a slow decrease in the intermediate regime, followed by a faster one when state $|2\rangle$ dominates (Fig. S6 of the Supplemental Material [26]).

**IV. SUMMARY AND CONCLUSION**

The above results underline the role of orbital physics in CeAu$_2$Si$_2$ and CeCu$_2$X$_2$. The critical end point, identified at $(p_c, T_c)$ through the scaling of the resistivity around $\rho^*$ in CeAu$_2$Si$_2$, as well as previously in CeCu$_2$Si$_2$ [12], can be
that of an orbital transition line, first described by Hattori [19] and in agreement with our calculations (see also Ref. [20]). In these systems, only a crossover regime is realized because the temperature \( T_{\sigma} \) is slightly negative. However, \( T_{\sigma} \) is small enough that the charge or orbital fluctuations associated with the orbital crossover are sufficiently developed to mediate both the non-Fermi liquid properties of the normal phase and the superconducting pairing. In CeAu\(_2\)Si\(_2\), magnetism and superconductivity may originate from the occupancy of different CF levels in the intermediate-pressure region according to our calculations. The increase of Kondo scale induced by the orbital transition may drive the collapse of magnetism, explaining its sudden disappearance and hence the proximity of the temperatures \( p_c \) and \( p^* \), as opposed to the case of CeCu\(_2\)Si\(_2\) for which these two pressures are well separated. As discussed in Sec. III B, it appears that spin fluctuations are not the driving force for superconductivity in CeAu\(_2\)Si\(_2\). Still, it remains challenging to understand the giant overlap of SC properties of the normal phase and the superconducting state, magnetism and superconductivity and in, particular, the striking relationship \( T_c \propto T_M \) observed in a broad pressure range, which definitely require further studies.

In conclusion, CeAu\(_2\)Si\(_2\) is discovered to be a new HF superconductor under a very broad pressure interval from 11.8 to 26.6 GPa. Within approximately two-thirds of this interval, SC appears below the magnetic phase transition. Intriguingly, when increasing pressure from 16.7 to 20.2 GPa, both bulk \( T_c \) and \( T_M \) are strongly enhanced, and almost proportional. \( T_c \) reaches its maximum value of \( \sim 2.5 \) K slightly below the pressure \( p_c \approx 22.5 \) GPa, where magnetic order disappears. The scaling behavior of resistivity indicates a continuous delocalization of Ce-4f electrons associated with a critical end point lying just above \( p_c \). The \( T_c \) maximum occurs when the Kondo and CF energies are similar and at almost the same unit-cell volume as for CeCu\(_2\)Si\(_2\) and CeCu\(_2\)Ge\(_2\), providing a clue to the pairing mechanism. First-principles calculations indicate the existence of an intermediate state in the Ce-4f orbital occupancy in CeAu\(_2\)Si\(_2\), which might be related to its peculiar behavior in comparison with its close relatives CeCu\(_2\)X\(_2\). Nevertheless, we emphasize that the understanding of the newly observed behavior in CeAu\(_2\)Si\(_2\) remains largely open [53]. Future experimental investigations of the isoelectronic compounds CeAg\(_2\)Si\(_2\), or even CeAu\(_2\)Ge\(_2\) and CeAg\(_2\)Ge\(_2\), will likely enrich the debate. On the theoretical side, calculations of various Ce-based systems are highly desirable in order to extend comparisons with the already rich experimental results. For example, an interesting issue is the very weak pressure response of the intermediate valence compound CePd\(_3\) [54].

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[33] Our estimates within the constrained LDA method for CeCu2Si2, CeCu2Ge2, and CeAu2Si2 give values of F0 differing by less than 0.2 eV. Hence, the value previously used for CeCu2Si2 has been adopted for the two other compounds.


[37] The phonon contribution ρph is well approximated by a linear-in-T term above ΘD/10, where ΘD is the Debye temperature. From specific heat data of Ref. [24], ΘD ≈ 270 K is obtained. Below ΘD/10 ≈ 27 K, the linear term overestimates ρph. However, the low-T resistivity is dominated by the magnetic contribution even at low pressure, and thus the subtraction of a small linear term has weak effect on our data analysis. Under pressure, ρph is expected to decrease slightly, but in comparison to the strong increase of the magnetic resistivity, it can be taken as pressure independent.


