Crystallographic and superconducting properties of the fully-gapped noncentrosymmetric 5$d$-electron superconductors Ca$M$Si$_3$ ($M = \text{Ir, Pt}$)

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We report crystallographic, specific heat, transport, and magnetic properties of the recently discovered noncentrosymmetric 5$d$-electron superconductors CaIrSi$_3$ ($T_c = 3.6$ K) and CaPtSi$_3$ ($T_c = 2.3$ K). The specific heat suggests that these superconductors are fully gapped. The upper critical fields are less than 1 T, consistent with limitation by conventional orbital depairing. High, non-Pauli-limited $\mu_0H_c^2$ values, often taken as a key signature of novel noncentrosymmetric physics, are not observed in these materials because the high carrier masses required to suppress orbital depairing and reveal the violated Pauli limit are not present.

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I. INTRODUCTION

There has been a great deal of interest in noncentrosymmetric superconductors initiated by the discovery of highly unconventional behavior in CePt$_3$Si$_3$ \[1\]. The overwhelming majority of superconductors studied to date have crystal structures exhibiting inversion symmetry. If an inversion element is present, inversion about the origin in momentum space can at most change the sign of the superconducting pairing function, which can thus be classified by its parity, and the spin state of the pairs must be either symmetric or antisymmetric (triplet or singlet) on exchange of the component fermions. In structures lacking an inversion element, however, there is no such constraint, parity is not a meaningful label, and pairing states cannot be classified as singlet or triplet. In such a material, spin-orbit terms can split the underlying band structure, and thus the Fermi surface, by spin orientation. Where the splitting is large compared to the superconducting gap, pairing is expected to occur only within each Fermi surface sheet, and since there is only one allowed spin orientation at any given point on each sheet, the pairing state will be a mixture of what would normally be regarded as singlet and triplet components. A wide variety of exotic superconducting properties have been predicted in noncentrosymmetric superconductors \[2,3\], but many have not yet been observed.

A number of other noncentrosymmetric superconductors have since been reported and are being actively studied, including UIr \[4\], CeRhSi$_3$ \[5\], Ir$_2$Ga$_9$ \[6\], and B-doped SiC \[7\]. Exotic properties, however, have so far mostly been observed in materials containing cerium, and cerium compounds commonly exhibit unusual magnetism; the magnetism and superconductivity are thought to originate from the same itinerant 4$f$ electrons. Disentangling the not-fully-understood, novel noncentrosymmetric physics from the complications introduced by strongly correlated $f$ electrons of heavy-fermion compounds remains a key challenge, and will require the study of non-magnetic, $f$-electron-free noncentrosymmetric superconductors. Thus far, the only $d$-electron systems in which unconventional behavior has been reported that might arise from the lack of inversion symmetry are Li$_2$Pt$_3$B \[10,11\] and LaNiC$_2$ \[12\].

Recently, nine new noncentrosymmetric superconductors were reported with the same crystal structure as CeRhSi$_3$ (space group $I4mm$) \[13,14\], with chemical formulas $AMSi_3$ ($A = \text{Ca, Sr, Ba}; M = \text{Co, Rh, Ir, Ni, Pd, Pt}$). All are thought to be non-magnetic, and none contain active $f$ electrons. These materials are uniquely valuable because they can be readily compared to Ce-containing superconductors with an identical crystal structure. Unlike their Ce-based analogs, in which superconductivity only emerges at high pressures once antiferromagnetism has been suppressed \[15,16\], the newly-discovered materials superconduct at ambient pressure. This is suggestive of a magnetic pairing mechanism for the Ce-based materials and a more conventional phonon mechanism for the new materials.

The new $f$-electron-free 1-1-3 silicides have the potential to be the subject of intense research. A key first step is basic characterization of the superconducting state. To this end, we prepared polycrystalline samples of the CaMSi$_3$ materials ($M = \text{Ir, Pt}$) that would be expected to have the strongest spin-orbit interactions and investigated their structure, specific heat, resistivity, and magnetic properties.

II. SAMPLE PREPARATION AND CHARACTERIZATION

Polycrystalline samples were prepared from CaSi (99.9\%, Furuuchi Chemical, 1-3 mm granule), Ir (99.99\%,
Furuuchi Chemical, powder), Pt (99.98%, Nilaco, powder), and Si (99.999%, Furuuchi Chemical, powder) by arc melting. The raw materials were ground under nitrogen to avoid oxidation, then pressed into a pellet, and melted under argon. Samples synthesized starting from the nominal composition of Ca:Ir:Si=1:1:3 produced the new material CaIr$_3$Si$_7$, discussed in the Appendix.

To compensate for loss of volatile calcium silicides, molar ratios of Ca:Ir:Si=3:1:4.7, and Ca:Pt:Si=3:1:5 were used. Powder x-ray diffraction (XRD) was performed with a commercial x-ray diffractometer (MAC Science, M03XHT$^{22}$) using CuK$_\alpha$ radiation (wavelength: 1.54056 Å), and surface analyses using a commercial scanning electron microscope (SEM, Keyence VE-9800S) and energy-dispersive x-ray spectrometer (EDX, EDAX VE7800), all at room temperature. The results are presented in Fig. 1. Both the CaIrSi$_3$ and CaPtSi$_3$ samples exhibited additional XRD peaks from impurity phases, but were of high enough quality that their superconducting properties could be investigated. The inset of Fig. 1 displays a SEM image. EDX composition mapping identified two distinct phases in the CaIrSi$_3$ sample, with approximate cation ratios Ca:Ir:Si = 1:1.03:2.95, consistent with CaIrSi$_3$, and Ca:Ir:Si = 1:0:2.28. The Ir-free phase did not appear in XRD, suggesting it to be solidified melt without a well-defined crystal structure.

Single phase CaIrSi$_3$ grains of size $\sim$200 µm were isolated using dilute hydrochloric acid, then crushed. Homogeneous micron-sized grains were selected using an ethanol suspension, then sealed in a Lindemann glass capillary of internal diameter 0.2 mm. High-resolution synchrotron XRD measurements were performed in transmission mode at the SPring-8 BL02B2 beam line using N$_2$ gas-flow temperature control and a large Debye-Scherrer camera with an imaging plate detector$^{18}$ which was set up to collect data from 0.010 to 78.68° in $\theta$, with a resolution of 0.010°. Data were collected at a series of temperatures from 90 to 300 K with exposure times of five minutes, and a higher-statistics dataset with a 60-minute exposure time was taken on a different sample at 100 K for structure refinement. The highest peak in the latter dataset had approximately 1,100,000 counts. An incident x-ray wavelength of 0.35747(1) Å was used, calibrated with a CeO$_2$ standard.

No technique was found that would result in single-phase CaPtSi$_3$ grains, but aqua regia dissolved most impurities, and it was also possible to isolate CaPtSi$_3$-free grains of the remaining impurity phases. Spectra with and without CaPtSi$_3$ were collected as for CaIrSi$_3$, using a wavelength of 0.351190(12) Å, but without a high-statistics dataset. By comparing the CaPtSi$_3$ and impurity-phase spectra, reflections associated with impurity phases could be deleted, allowing structure refinements for CaPtSi$_3$ as shown in Fig. 1. The previously mentioned limitations require that the CaPtSi$_3$ XRD results be treated with caution, but they should provide a useful starting point.
tonically with temperature by less than 0.4% over the temperature range probed, as displayed in Fig. 2 for CaIrSi$_3$. In this compound only, a small slope change in the c-axis lattice parameter can be seen at 200 K, and the c-axis position of the Si(2) (Ir–Si layer) site appears to fall by about 0.005 Å above this temperature, making the Ir–Si layer slightly flatter. The above changes were reflected in the interatomic distances.

Figure 3 and Table I report the results of a Rietveld structure refinement performed on the higher-statistics CaIrSi$_3$ data using the program Synchrotron-Powder [19], using 1086 reflections from 2.500 to 75.000°. The reliability factors based on the weighted profile, $R_{wp}$, and on the Bragg intensities, $R_I$, were 4.30% and 1.98%, respectively. Refinements of the temperature-dependent CaPtSi$_3$ data typically produced reliability factors $R_{wp}$ and $R_I$ of 4.8–5.1% and 7.0–8.5%, respectively. The results of the refinement at 100 K are reported in Table II.

![Figure 3](image-url) (Color online) The Rietveld structure refinement of CaIrSi$_3$ performed on the higher-statistics synchrotron x-ray data at 100 K.

### III. SUPERCONDUCTING PROPERTIES

#### A. Dc susceptibility and resistivity

Using polycrystalline samples, dc susceptibility measurements were performed with a commercial Superconducting Quantum Interference Device (SQUID) magnetometer (Quantum Design, MPMS-XL) down to 1.8 K, and resistivity measurements were performed with a commercial instrument (Quantum Design, PPMS) with a $^3$He refrigeration insert down to 0.35 K using a conventional four-probe technique. Resistivity in zero field up to 300 K for each compound is exhibited in Figs. 4 (a) and 4 (b). The temperature dependence of the resistivity indicates typical metallic behavior with residual resistivity ratios (RRR, $\rho_{300K}/\rho_{5K}$) of $\sim$4 for CaIrSi$_3$ and $\sim$1.6 for CaPtSi$_3$. The low-temperature resistivity and the dc susceptibility in 1 mT for each compound, presented in Figs. 4 (c) and 4 (d), exhibit clear superconducting transitions at 3.7 K for CaIrSi$_3$ and 2.3 K for CaPtSi$_3$. For CaIrSi$_3$ the transition temperature is approximately 20% higher than that reported in Ref. [20], attributed to improved sample quality.

The volume fractions estimated from zero field cooled dc susceptibility data were $\sim$170% for CaIrSi$_3$ and $\sim$100% for CaPtSi$_3$, assuming the samples to be single phase. These large volume fractions are attributed to neglecting demagnetizing effects, but suggest that a majority of each sample was superconducting. The large difference between field-cooled and zero-field-cooled data is likely due to the presence of melt inclusions that can trap magnetic flux. The RRRs and volume fractions indicate that CaIrSi$_3$ was higher quality than CaPtSi$_3$, consistent with the XRD result.

#### B. Specific heat

Specific heat measurements were performed down to 0.35 K using a relaxation-time-method calorimeter (Quantum Design, PPMS) on a $^3$He refrigeration insert. The total specific heat for each compound is presented in Figs. 5 (a) and 5 (b), and the electronic specific heat

| Table I. The lattice parameters, fractional atomic coordinates, and interatomic distances of CaIrSi$_3$ at 100 K. $U$(iso) is the isotropic thermal displacement parameter. |
|---|---|---|---|---|
| Refinement | Space group | Tetragonal, $I4mm$ (No. 107) | |
| Z / Calculated density | 2 / 6.085 Mg/m$^3$ | |
| Absorption coefficient | 5.732 mm$^{-1}$ | |
| Data / restraints / parameters | 1086 / 0 / 16 | |
| Lattice parameters (Å) | | |
| $a$ | 4.18327(2) | |
| $c$ | 9.87278(7) | |
| Fractional Coordinates | | |
| $x$ | 0.00000 | 0.00000 | 0.00000 | 0.00489(24) |
| $y$ | 0.00000 | 0.00000 | 0.64666(15) | 0.00247(2) |
| $z$ | 0.00000 | 0.00000 | 0.40975(29) | 0.00451(35) |
| $U$(iso) (Å$^2$) | 0.25886(18) | 0.00451(35) |
| Interatomic distances (Å) | | |
| Ir–Si(1) | 2.3396(1) | |
| Ir–Si(2) | 2.3674(1) | |
| Si(1)–Si(2) | 2.5669(1) | |
| Ca–Si(1) | 3.0897(1) | |
| Ca–Si(2) | 3.1687(1) | |
| Ca–Ir | 3.2931(1) | |


TABLE II. Lattice parameters, fractional atomic coordinates and interatomic distances for CaPtSi$_3$ at 100 K; $U_{\text{iso}}$ is the isotropic thermal displacement parameter.

| Refinement | Space group | $Z$, Calculated density | Absorption coefficient | Data / restraints / parameters |
|------------|-------------|-------------------------|------------------------|-------------------------------|
|            | Tetragonal, $I4/mmm$ (No. 107) | 2, 6.133 Mg/m$^3$ | 5.683 mm$^{-1}$ | 149 / 0 / 5 |

| Lattice parameters (Å) | Fractional Coordinates | Interatomic distances (Å) |
|------------------------|------------------------|---------------------------|
| $a$ 4.19880(10) | $x$ $y$ $z$ $U_{\text{iso}}$ (Å$^2$) | Pt–Si(1) 2.427(14)  |
| $c$ 9.8111(4) | | Pt–Si(2) 2.383(5)  |
| | Ca–Si(1) 3.141(4)  |
| | Ca–Si(2) 3.172(6)  |
| | Ca–Pt 3.283(3)  |

The only two free parameters in this procedure are $T_c$ and the superconducting contribution to the electronic specific heat coefficient $\gamma_s$. The data are fit up to a $T/T_c$ of just over 70%, and agree well with the BCS curve in this region. The fits result in $T_c$ values of 3.44 K for CaIrSi$_3$ and 2.1 K for CaPtSi$_3$, and $\gamma_s$ coefficients of 4.0 mJ/mol K$^2$ for CaIrSi$_3$ and 2.1 mJ/mol K$^2$ for CaPtSi$_3$. Entropy conservation at the specific heat jump of each compound gives the same $T_c$ (see Figs. 5 (c) and 5 (d)). These values of $T_c$ correspond to an average of the $T_c$ distribution in each sample. The superconducting fraction of each sample is estimated from $\gamma_n/\gamma_s$ to be $\sim 70\%$ in CaIrSi$_3$ and $\sim 55\%$ in CaPtSi$_3$, consistent with earlier indications that the CaPtSi$_3$ sample contained a greater proportion of impurity phase. The thermodynamic critical field $\mu_0H_c(0)$ is estimated using $\mu_0H_c^2(0)/2 = -\gamma_s T_c^2/2 + T_c/\int_{0}^{T_c} c_{el,s}(T)dT$, where $c_{el,s}(T)$ is the electronic specific heat in the superconducting phase, to be 0.023 T for CaIrSi$_3$ and 0.0094 T for CaPtSi$_3$. 

in Figs. 5 (c) and 5 (d). These were calculated assuming the molar weight of the target phases. Superconductivity in both compounds was suppressed by a magnetic field of 1 T. The normal-state specific heat was found to be invariant under external magnetic fields, so the normal-state electronic specific heat coefficients $\gamma_n$ and the lattice specific heat coefficients $\beta$ were deduced from the data in 1 T by a least-squares fit of the total specific heat $c_P$ to $\gamma_n T + \beta T^3$. This results in $\gamma_{n,\text{Ir}} = 5.8$ mJ/mol K$^2$ and $\beta_{\text{Ir}} = 0.21$ mJ/mol K$^4$ for CaIrSi$_3$, and $\gamma_{n,\text{Pt}} = 4.0$ mJ/mol K$^2$ and $\beta_{\text{Pt}} = 0.20$ mJ/mol K$^4$ for CaPtSi$_3$. The Debye temperature $\Theta_D$ of each compound is estimated from $\beta = (12/5)\pi^4 N_A k_B / \Theta_D^3$ as 360 K for CaIrSi$_3$ and 370 K for CaPtSi$_3$, comparable to those found in ordinary metals. Here $N_A = 5$ is the number of atoms per formula unit, $N_A$ is Avogadro’s number and $k_B$ is Boltzmann’s constant. From the specific heat heasets, we define the transition temperatures $T_c = 3.6$ K for CaIrSi$_3$ and 2.3 K for CaPtSi$_3$ in zero field, consistent with those from dc susceptibility and resistivity. The specific heat jumps indicate the superconductivity to be bulk in nature.

As presented in Figs. 5 (c) and 5 (d), the electronic specific heat coefficient $\gamma$ converges to a finite value at low temperatures even in zero field. This indicates that normal state conduction electrons that do not participate in the superconductivity persist at the Fermi level down to 0 K. However, it cannot be distinguished whether these electrons are contained in CaIrSi$_3$ (CaPtSi$_3$) or in impurity phases.

A fit of $c_{el}$ to a polynomial approximation to the conventional weak coupling BCS curve tabulated numerically in Ref. [21] is also displayed in Figs. 5 (c) and 5 (d). The only two free parameters in this procedure are $T_c$ and the superconducting contribution to the electronic specific heat coefficient $\gamma_s$. The data are fit up to a $T/T_c$ of just over 70%, and agree well with the BCS curve in this region. The fits result in $T_c$ values of 3.44 K for CaIrSi$_3$ and 2.1 K for CaPtSi$_3$, and $\gamma_s$ coefficients of 4.0 mJ/mol K$^2$ for CaIrSi$_3$ and 2.1 mJ/mol K$^2$ for CaPtSi$_3$. Entropy conservation at the specific heat jump of each compound gives the same $T_c$ (see Figs. 5 (c) and 5 (d)). These values of $T_c$ correspond to an average of the $T_c$ distribution in each sample. The superconducting fraction of each sample is estimated from $\gamma_n/\gamma_s$ to be $\sim 70\%$ in CaIrSi$_3$ and $\sim 55\%$ in CaPtSi$_3$, consistent with earlier indications that the CaIrSi$_3$ sample contained a greater proportion of impurity phase. The thermodynamic critical field $\mu_0H_c(0)$ is estimated using $\mu_0H_c^2(0)/2 = -\gamma_s T_c^2/2 + T_c/\int_{0}^{T_c} c_{el,s}(T)dT$, where $c_{el,s}(T)$ is the electronic specific heat in the superconducting phase, to be 0.023 T for CaIrSi$_3$ and 0.0094 T for CaPtSi$_3$. 

![Image of graph](image-url)
FIG. 5. (Color online) Temperature dependence of total specific heat $c_P$ for (a) CaIrSi$_3$ and (b) CaPtSi$_3$, and electronic specific heat $c_{el}$ for (c) CaIrSi$_3$ and (d) CaPtSi$_3$. $T_c$ onsets in 0 T are 3.6 K for CaIrSi$_3$ and 2.3 K for CaPtSi$_3$, and in 0.1 T are 2.5 K for CaIrSi$_3$ and 1.7 K for CaPtSi$_3$. Solid lines are BCS fits. The shaded regions have the same area on either side of the specific heat jump, corresponding to entropy conservation. The $T_c$ values from this procedure match with those from the BCS fits.

C. Magnetic phase diagram

Measurements of ac susceptibility in various magnetic fields were performed by a mutual-inductance method (1 $\mu$T, 3011 Hz) down to 0.3 K using a commercial 3He refrigerator (Oxford Instruments, Heliox), equipped with a superconducting magnet. These and the resistivity results are presented in Fig. 6. The ac susceptibility measurements were performed on both warming and cooling with no hysteresis; thus, only the warming results are displayed. Under magnetic fields, ac susceptibility onsets were observed up to 0.27 T for CaIrSi$_3$ and 0.15 T for CaPtSi$_3$, and resistivity onsets up to 0.6 T for both compounds: several times larger than the thermodynamic critical fields. The large critical fields and nonhysteretic transition temperatures clearly indicate that these compounds are type-II superconductors.

The $H - T$ phase diagrams of CaIrSi$_3$ and CaPtSi$_3$ deduced from the ac susceptibility $\chi'_{ac}$ onset, resistivity $\rho$ onset, and specific heat $c_P$ onset are summarized in Fig. 7. The $T_c$ onsets were defined as 5% of full, zero-field diamagnetism in $\chi'_{ac}$, a 5% decrease in $\rho$, and the onset in $c_P$. We note that for CaPtSi$_3$ the transition broadens substantially under magnetic fields. This behavior is correlated with the phase purity of the sample as evidenced by impurity peaks in XRD and the larger residual contribution in the specific heat. Each curve is remarkably linear and is slightly concave upward in low magnetic fields. In neither system do the curves deduced from the $\chi'_{ac}$ and $\rho$ onsets coincide, and the discrepancy between them is more prominent for CaPtSi$_3$ than for CaIrSi$_3$.

Since the $H - T$ curve of CaIrSi$_3$ based on $\chi'_{ac}$ onset begins to saturate at high fields, $\mu_0 H_{c2}(0)$ is estimated from the points at 0.3 K as a lower limit and the linear extrapolation to zero temperature as an upper limit: 0.27 – 0.32 T. Similarly for CaPtSi$_3$ it is estimated as 0.15 – 0.20 T. Approximate Ginzburg-Landau parameters $\kappa_{GL}$, superconducting coherence lengths $\xi(0)$, and penetration depths $\lambda(0)$ are estimated from the $\mu_0 H_{c2}$ lower limits with the relations $\mu_0 H_{c2}(0) = \sqrt{2\kappa_{GL}\Phi_0 H_{c}(0)}$, $\mu_0 H_{c2}(0) = \Phi_0/2\pi\xi^2(0)$, and $\kappa_{GL} = \lambda(0)/\xi(0)$, respectively. These results should be treated with caution since they come from multiphase, polycrystalline samples of anisotropic materials, but they provide an essential starting point. The results are summarized in Table III with the other physical properties determined in this study.

IV. DISCUSSION AND CONCLUSION

The specific heat results are generally well explained by weak-coupling BCS theory and similar to reports on BaPtSi$_3$ [14]. While the agreement with the BCS curve suggests that these superconductors are fully gapped, the
TABLE III. Physical properties of polycrystalline CaIrSi$_3$ and CaPtSi$_3$. Superconducting parameters $\kappa_{GL}$, $\xi(0)$, and $\lambda(0)$ are based on the lower limits of $\mu_0H_{c2}(0)$ determined from $\chi'_{ac}$ onset. Note that these values could be affected by sample quality, and in some cases should be anisotropic.

|                  | CaIrSi$_3$ | CaPtSi$_3$ |
|------------------|------------|------------|
| $T_c$            | 3.6 K      | 2.3 K      |
| $\mu_0H_{c2}(0)$ ($\chi'_{ac}$ onset) | 0.27 T | 0.15 T |
| $\mu_0H_{c1}(0)$ | 0.023 T   | 0.0094 T  |
| $\kappa_{GL}$   | 8.3        | 11         |
| $\xi(0)$        | 34 nm      | 47 nm      |
| $\lambda(0)$    | 280 nm     | 520 nm     |
| $\gamma_n$      | 5.8 mJ/mol K$^2$ | 4.0 mJ/mol K$^2$ |
| $\gamma_s$      | 4.0 mJ/mol K$^2$ | 2.1 mJ/mol K$^2$ |
| $\Theta_D$      | 360 K      | 370 K      |

specific heat of CaIrSi$_3$ falls below this curve just above $0.7T_c$. Although the superconducting transition is broad, this is well outside the transition width. This deviation is suggestive of a departure from a pure s-wave gap structure, as in a multiband or anisotropic-gap scenario, the alternative being an unusual distribution of $T_c$ with a significant tail to low temperatures. The apparent full gap strongly suggests that the superconducting pairing is dominantly or exclusively singlet; a triplet component could introduce gap anisotropy.

The experimental values of $\mu_0H_{c2}(T)$ are much smaller than the Pauli-limiting fields $\mu_0H_p(0)$ of 1.84T$_c$ expected in weak-coupling s-wave BCS theory, $\sim$6.5 T for CaIrSi$_3$ and $\sim$4 T for CaPtSi$_3$. Barring large corrections to $\mu_0H_p$, the dominant pair-breaking effect in CaIrSi$_3$ and CaPtSi$_3$ would be orbital depairing. This represents a significant difference from the Ce-containing isostructural superconductors CeRhSi$_3$, CeIrSi$_3$, and CeCoGe$_3$, in which heavy-fermion masses strongly suppress orbital depairing to reveal that Pauli-limiting behavior does not set in where expected for a singlet condensate. Pauli pair breaking is strongly suppressed by the presence of a triplet component or a van Vleck-like susceptibility specific to noncentrosymmetric systems [4, 16, 17, 22]. Unless orbital depairing is also suppressed, however, an extremely high $\mu_0H_{c2}(0)$ that violates conventional expectations for the Pauli limit, commonly used as a key signature of novel noncentrosymmetric physics, will not be exhibited. This is the case in CaIrSi$_3$ and CaPtSi$_3$, whose small $\gamma$ values indicate light carrier masses and in which orbital depairing is not suppressed.

In both samples, the $\mu_0H_{c2}(T)$ obtained from the ac susceptibility and resistivity onset differs substantially. This discrepancy far exceeds the factor of 1.695 associated with $\mu_0H_{c3}$ surface superconductivity and thin limit physics, so other effects must be involved. One possible scenario is that anisotropic superconducting parameters, expected given the tetragonal crystal structure, lead to an upper critical field with a strong, narrow peak for one field direction, producing very low volume fractions of robust superconductivity. Another possibility is pressure enhancement of the superconductivity at grain boundaries due to thermal expansion, leading to very thin superconducting surface layers offering a pathway for conductivity but with negligible volume fraction. Finally, the samples could contain networks of more-defective material with almost no volume fraction, in which the mean free path $\ell$ is shorter than the intrinsic $\xi_0$. In such a region, the effective coherence length $\xi = (1/\xi_0 + 1/\ell)^{-1}$ is limited by $\ell$, increasing $\mu_0H_{c2} \sim 1/\xi^2$. This would also help to explain a discrepancy with our earlier image furnace-grown CaIrSi$_3$ samples [20], which have a significantly lower $T_c$ and higher $\mu_0H_{c2}(0)$. If $\xi$ in the majority of the samples in the present study is dominated by the change in $\xi_0$, which decreases with decreasing $T_c$, the broadening of the transition in $\chi_{ac}$ can also be coherently explained. The data currently available do not permit determining which of these effects contribute or are dominant. Settling these issues will require single-crystalline samples — anisotropy in the superconducting parameters would be readily apparent when varying the field angle, pressure effects could be studied, and magnetic and non-magnetic impurities could be doped in to test their effect controllably.

An upward curvature in low fields and striking linearity of $\mu_0H_{c2}(T)$ are observed in both compounds. Such behavior is quite uncommon, but has been observed
in multiband superconductors, for example, MgB$_2$. With the full crystal structure determined in CaIr$_3$Si$_7$ and CaPt$_3$Si$_3$, band-structure calculations may now be performed to predict the shape of the Fermi surface and whether multiband physics is likely to play a role. This is noteworthy since, to the authors’ knowledge, atomic positions have never been published for the Ce analog, although they have been for LaIr$_3$Si and LaRh$_3$Si$_7$, nonsuperconducting CePt$_3$Si$_3$, and BaPt$_3$Si$_3$.

One somewhat surprising result is that CaIr$_3$Si$_7$, CaPt$_3$Si$_3$ and previously published BaPt$_3$Si$_3$ all behave in a very similar fashion. The only clear qualitative differences are in the transition widths and the magnitude of the difference between the $T_c$ onsets. Because the spin-orbit coupling strength is expected to increase strongly with atomic number, all three materials are expected to exhibit strong band splitting. Although the Pt-based materials should have somewhat stronger band splitting, its effect on the physical properties will hinge on details of the band structure. In order to determine whether or not noncentrosymmetric physics is operative in these materials, microscopic techniques such as nuclear magnetic resonance or $\mu$SR may prove useful.

In conclusion, we reported the crystallographic and superconducting properties of CaIr$_3$Si$_7$ and CaPt$_3$Si$_3$. The electronic specific heat coefficients $\gamma$ are a few mJ/mol K$^2$ in both CaIr$_3$Si$_7$ and CaPt$_3$Si$_3$, values not unusual for metals, indicating that the electron correlations are not strong in these compounds. Their specific heat results suggest that these superconductors are fully gapped. The upper critical fields $H_{c2}(0)$ are less than a Tesla and consistent with a conventional orbital depairing mechanism. This and the small $\gamma$ values, constitute a significant departure from the heavy fermion Ce-based materials. Because several results have multiple possible interpretations and the role of anisotropy is unclear, single-crystalline samples will be required. Our results on the promising 5d-electron analogs of known Ce-based materials lay the groundwork for studies of the importance of heavy electrons in noncentrosymmetric superconductors.

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Appendix A: The new material CaIr$_3$Si$_7$

While optimizing the preparation technique for CaIr$_3$Si$_7$, the previously unreported ternary phase CaIr$_3$Si$_7$ was discovered, and subsequently reproduced by solid-state reaction of Ca:Ir:Si = 1:1:3 under vacuum in a sealed quartz tube (1100 °C, 24 hours). This compound crystallizes in the rhombohedral space group $R3c$ (No. 167), isotypic to ScRh$_3$Si$_7$ and ScIr$_3$Si$_7$, and possesses an inversion center. It does not exhibit superconductivity above 1.8 K. We note that thorough investigation of the synthesis of CaPt$_3$Si$_3$ by a flux method by Takeuchi et al., resulted in synthesizing a new centrosymmetric superconductor, Ca$_2$Pt$_3$Si$_5$.

A single-crystalline grain of CaIr$_3$Si$_7$, prepared by melting a mixture of stoichiometry Ca:Ir:Si = 1:1:3 in an image furnace, was separated from excess melt phases using dilute hydrochloric acid. This grain was then characterized at room temperature by single-crystal x-ray diffraction at SPring-8 beam line BL02B1 using a large cylindrical image plate detector. A wavelength of 0.35100 Å was used, and data were collected over the index range $0 \leq h \leq 16$, $0 \leq k \leq 16$, and $0 \leq l \leq 49$, and over a range in $\theta$ of 1.83 to 26.02°. A total of 1816 reflections were collected, all of which were unique and 1697 of which had intensity $>2\sigma(I)$. The structure was solved and refined using SHELX97 and SHELXL07, respectively. results are summarized in Table IV. Refinement was by a full-matrix least-squares minimization of $F^2$. The final reliability factors $R_1$ and $wR_2$ were 2.04% and 7.11%, respectively, on peaks with intensity greater than $2\sigma(I)$, and 2.70% and 7.93%, respectively, on all data.

FIG. 8. (Color online) Crystal structure of CaIr$_3$Si$_7$ as determined by single-crystal x-ray diffraction.

Since this crystal structure contains a large number of atoms per unit cell in a nontrivial arrangement, it must...
TABLE IV. Crystal data and structure refinement parameters of CaIr$_3$Si$_7$ at 100 K. The equivalent isotropic displacement parameter $U_{\text{eq}}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| Parameter                                      | Value                  |
|------------------------------------------------|------------------------|
| Space group                                    | Rhombohedral, $R3c$ (No. 167) |
| Z / Calculated density                         | 6 / 8.143 Mg/m$^3$     |
| Absorption coefficient                         | 33.609 mm$^{-1}$       |
| Data / restraints / parameters                  | 1816 / 0 / 20          |
| Extinction coefficient                          | 0.00016(15)            |
| Lattice parameters (Å)                          |                        |
| $a$                                             | 7.5782(3)              |
| $c$                                             | 20.0091(2)             |
| Fractional Coordinates                          |                        |
| $x$ $y$ $z$ $U_{\text{eq}}$ (Å$^2$)             |                        |
| Ir                                              | 0.346499(17) 0.013165(17) 0.08333 0.00205(3) |
| Ca                                              | 0.00000 0.00000 0.00000 0.00308(10) |
| Si(1)                                           | 0.46234(11) 0.14240(11) -0.02962(4) 0.00338(8) |
| Si(2)                                           | 0.66667 0.33333 0.08333 0.00237(17) |
| Interatomic distances (Å)                       |                        |
| Ir–Si(2)                                        | 2.42630(13)            |
| Ir–Si(1)                                        | 2.4449(7)              |
| Ir–Si(1)                                        | 2.4526(7)              |
| Ir–Si(1)                                        | 2.5201(7)              |
| Ir–Ca                                          | 3.0697(1)              |
| Ca–Si(1)                                        | 3.1257(7)              |
| Si(1)–Si(1)                                     | 2.5985(13)             |
| Si(1)–Si(2)                                     | 2.7127(7)              |
| Si(1)–Si(1)                                     | 2.7365(15)             |
| Si(1)–Si(1)                                     | 2.7605(15)             |

Refinement

As ScRh$_3$Si$_7$, it was portrayed as an array of Sc(Ca)-centered Rh(Ir) octahedra and Si double tetrahedra in which the shared apex was the Si(2) site. However, since the shortest bonds in the material are those between Rh(Ir) and Si, it may be more realistic to visualize the structure in terms of slightly twisted Si-centered Ir$_3$Si$_7$ barrels and isolated Ca atoms. A crystal structure based on this scheme is presented in Fig. 8.

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