Exploring hidden order through Co and Ir substitution in URu$_2$Si$_2$

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We report results on the substitution of Co and Ir at the Ru site in the URu$_2$Si$_2$ compound. Measurements of x-ray diffraction, electrical resistivity, dc magnetic susceptibility, and specific heat were performed on polycrystal samples of URu$_{2-x}M_x$Si$_2$ for $M = \text{Co, Ir}$ at low concentrations up to $x = 0.10$. The features in the specific heat and electrical resistivity were used to construct $T-x$ phase diagrams in which the “hidden order” (HO) and superconducting phases are suppressed with increasing $x$ in both systems. Based on theoretical models of electrical resistivity and specific heat, we extracted the value of the energy gap $\Delta$ that forms over a portion of the Fermi surface during the phase transition to “hidden order” (HO) at 17.5 K; we found that as $x$ is increased in both the Co- and Ir-substituted systems, $\Delta$ is suppressed faster than the HO phase leading to a possible “gapless” HO phase.

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I. INTRODUCTION

Uranium-based heavy-fermion materials are known for exhibiting complex behavior including the combination of superconductivity with various types of magnetic behavior such as ferromagnetism, antiferromagnetism, spin fluctuations, and enhanced susceptibility.\textsuperscript{1} The URu$_2$Si$_2$ unit cell volume is unique among the members of this class of materials owing to the existence of an ordered phase for which the nature of the order parameter and elementary excitations is yet to be determined. This so-called “hidden order” (HO) phase occurs at a transition temperature of $T_{\text{HO}} = 17.5$ K and coexists with a superconducting phase with a transition temperature of $T_{\text{SC}} = 1.5$ K. The unconventional superconductivity is believed to be mediated by magnetic interactions and is (uncharacteristically) fully contained within the ordered (HO) phase.

Figure 1 displays those elements in the periodic table that are adjacent to Ru. The substituent elements $M = \text{Mn, Tc, Re, Fe, Os, Co, Rh, and Ir}$ may be substituted for Ru in URu$_2$Si$_2$ to form pseudoternary complexes URu$_{2-x}M_x$Si$_2$. Substitutions from the blue column to the left with $M = \text{Mn, Tc, Re}$ result in hole doped ($h^+$) ferromagnetic (FM) systems.\textsuperscript{2–6} Substitutions from the red column to the right with $M = \text{Co, Rh, and Ir}$ result in electron doped ($e^-$) antiferromagnetic (AFM) systems.\textsuperscript{3,7–9} Isoelectronic substitutions with $M = \text{Fe and Os}$ result in antiferromagnetic systems and mimic the effect of pressure.\textsuperscript{10–12} Various $M$ substitutions may result in a significant reduction ($V^-$) or expansion ($V^+$) of the unit cell volume. A unit cell for the pseudoternary complex URu$_{2-x}M_x$Si$_2$ is displayed in Fig. 1 in which the substituent atom $M$ (red ball) replaces the Ru atom (orange ball). In this article we address the effects of substituting $M = \text{Co and Ir}$ for Ru in URu$_2$Si$_2$ at concentrations up to $x = 0.10$. At these low concentrations of Co and Ir, there is no emergent (anti)ferromagnetic phase; however, it is known from a related study of both the URu$_{2-x} \text{Co}_x$Si$_2$ and URu$_{2-x} \text{Ir}_x$Si$_2$ systems at higher concentrations\textsuperscript{13} of Co and Ir, there are emergent antiferromagnetic phases similar to what was observed for the Rh-substituted system.

In this article, we report physical properties measurements performed on polycrystalline samples of both the URu$_{2-x} \text{Co}_x$Si$_2$ and URu$_{2-x} \text{Ir}_x$Si$_2$ systems at concentrations up to $x = 0.10$. Electrical resistivity and specific heat measurements reveal the moderate (slight) suppression of the transition temperature $T_{\text{HO}}$ with increasing Co (Ir) concentration. At lower temperature, the electrical resistivity reveals a significant reduction in the onset of superconductivity with increasing concentration in both the Co- and Ir-substituted compounds. At higher temperatures, measurements of electrical resistivity and magnetization reveal a slight enhancement in the onset of lattice coherence in the paramagnetic state as $x$ is initially increased up to $x = 0.10$.

We extracted the magnitude of the energy gap $\Delta$ from both the electrical resistivity $\rho(T)$ data and specific heat $C(T)$ data for the URu$_{2-x} \text{Co}_x$Si$_2$ and URu$_{2-x} \text{Ir}_x$Si$_2$ systems. We found that the energy gap associated with the HO phase transition in both the URu$_{2-x} \text{Co}_x$Si$_2$ and URu$_{2-x} \text{Ir}_x$Si$_2$ systems was rapidly suppressed leading to a possible “gapless” HO phase in which $\Delta$ is suppressed to zero K at finite non-zero transition temperature $T_{\text{HO}}$. The ratio of the energy gap to the transition temperature $T_{\text{HO}}$ is reduced by a factor of three in both the Co-substituted and Ir-substituted systems at a concentration of $x = 0.10$. A scenario of “gapless” HO was recently reported in an investigation of the Rh-substituted URu$_2$Si$_2$ compound in which the suppression of a “gapless” HO phase toward 0 K leads to a possible quantum critical point. Throughout this article we will compare the results reported herein for the Co and Ir-substituted URu$_2$Si$_2$ systems with those of other reports on the effects of doping at the Ru site, with particular at-
tention given to the Rh-substituted URu$_2$Si$_2$ compound owing to the similarity in the atomic electronic structure between the Co, Rh, and Ir elements. Finally, upon a modest increase in the substitution of Co and Ir for Ru, we speculate on the cause for the disruption of the HO phase to be an increase in the hybridization between the intermetallic d-electron bands and the f-electron bands of the U atoms.

![Diagram](image)

**FIG. 1:** (Left) Elements $M = \text{Mn, Tc, Re, Fe, Os, Co, Rh, and Ir}$ that are adjacent to Ru in the periodic table; $M$ is substituted for Ru to form pseudoternary complexes $\text{URu}_2-xM_x\text{Si}_2$. (Right) A ball and stick model of the body-centered-tetragonal unit cell for URu$_2$Si$_2$ is shown. The substituent atom $M$ (red ball) replaces the Ru atom (orange ball) to form the $\text{URu}_2-xM_x\text{Si}_2$ compound. In this article we examine the $\text{URu}_2-xM_x\text{Si}_2$ systems with $M = \text{Co and Ir}$.

II. EXPERIMENTAL DETAILS

Polycrystalline samples were synthesized from stoichiometric ratios of depleted U ingots (Argonne National Lab), Ru powder (Alfa Aesar 99.99+%), Ir sponge (99.99%), Co ingots (Alfa Aesar 99.9%), and Si chunks (99.999995%). The elements were arc-melted (four times) on a water-cooled copper hearth under an Ar atmosphere with a Zr getter. The samples were then annealed in quartz tubes under a 150 Torr Zr gettered Ar atmosphere with a Zr getter. The samples were then annealed in quartz tubes under a 150 Torr Zr gettered Ar atmosphere for 7 days at 900°C. The crystal structure was determined using x-ray powder diffraction (XRD) on a Bruker D8 Discover x-ray diffractometer with Cu-K radiation. The diffraction patterns were analyzed via Rietveld refinements using the GSASII software$^{14}$. The polycrystals were shaped and polished into rectangular bars and then sputtered with gold before gold wires were affixed to the sample with (Epo-tek H20E) silver epoxy. Electrical resistance was measured with a Linear Research LR-700 ac resistance bridge with a maximum excitation current of 10 mA using a standard four wire technique upon warming from 1.2 to 280 K in a custom He cryostat. Measurements of DC magnetic susceptibility were performed between 2 and 300 K in varying magnetic fields using a Quantum Design magnetic properties measurement system (MPMS). Specific heat measurements were carried out at temperatures down to 1.8 K with a Quantum Design physical properties measurement system (PPMS DynaCool).

III. RESULTS

A. X-ray diffraction

URu$_2$Si$_2$ exhibits a body-centered-tetragonal (bct) ThCr$_2$Si$_2$-type crystal structure (space group No. 139, $I4/mmm D_{4h}^{17}$).$^{15}$ The unit cell shown in Fig. 1 consists of alternating layers of Ru-Si planes and planes of U atoms. Previous reports indicate that the substitution of $M = \text{Rh, Fe, Os, and Re}$ for Ru does not significantly distort the crystal structure. The x-ray diffraction (XRD) results for several polycrystal samples from the $\text{URu}_2-xM_x\text{Si}_2$ system at various $x$ are displayed in Fig. 2(a). Over the range $40 \geq 2\theta \geq 79$, there is little variation in the intensity for the $\text{URu}_2-x\text{Co}_x\text{Si}_2$ system as the Co concentration is increased up to $x \leq 0.1$, indicating that for small substituent concentrations, there is no distortion to the lattice. The XRD results for the $\text{URu}_2-x\text{Ir}_x\text{Si}_2$ system were also unchanged as the Ir concentration was increased up to $x = 0.10$. Furthermore, the Rietveld refinements performed at concentrations ($x \leq 0.1$) for both the Co- and Ir-substituted systems, indicated that no significant impurity phases were detected. Figure 2b displays a representative Rietveld refinement for Co at $x = 0.07$.

The $a$ and $c$ lattice constants for both the Co and Ir-substituted samples are plotted as a function of $x$ and compared with the results for the $\text{URu}_2-xM_x\text{Si}_2$ compound substituted with $M = \text{Rh, Fe,}$ and $\text{Re}$.$^{11}$ The linear $x$ dependence for both the $a$ and $c$ lattice constants in the $\text{URu}_2-x\text{Co}_x\text{Si}_2$ and $\text{URu}_2-x\text{Ir}_x\text{Si}_2$ systems, respectively, is consistent with Vegard’s law in the low concentration limit. In the Co-substituted compound, the $a$ lattice parameter decreases monotonically with $x$ while the $c$ lattice parameter does not change significantly; in the Ir-substituted compound, there is a slight decrease in the $a$ lattice parameter in contrast to the noticeable increase in the $c$ lattice parameter with increasing $x$. The ratio of the lattice parameters $c/a$, displayed in Fig. 3(c), increases with increasing $x$ for all substitutions $M = \text{Co, Ir, P, Fe,}$ and $\text{Rh}$ with the largest rate of increase occurring in the Co-substituted system while the least rate of increase occurs in the Fe-substituted system.

B. Electrical Resistivity

The temperature dependence of the electrical resistivity $\rho(T)$ was measured in the basal plane parallel to the $a$ direction (see Fig. 1) for the $\text{URu}_2-xM_x\text{Si}_2 (M = \text{Co, Ir})$ systems upon warming from 1.2 to 270 K.
FIG. 2: (a) Several x-ray diffraction patterns for the URu$_{2-x}$Co$_x$Si$_2$ system with $x = 0.02$, 0.04, and 0.06 are shown over the interval $40 < 2\theta < 79$. The intensity patterns have been offset by a constant value for comparison. There is very little variation in the profile of the XRD intensity over the concentration range $0 \leq x \leq 0.1$ for Co. (b) A representative example of the Rietveld refinement for the URu$_{1.93}$Co$_{0.07}$Si$_2$ sample shown over the same range of $2\theta$. The black crosses represent the experimental data; the red line represents the fit of the Rietveld refinement to the data; the blue line represents the difference between the Rietveld refinement fit and the experimental data; and the expected $2\theta$ values of the Bragg reflections for the space group No. 139, $I4/mmm D_{4h}^{17}$ are indicated by the green arrows.

and is displayed in Fig. 4. Each of the $\rho(T)$ curves for the Co-substituted compound displayed in Fig. 4(a) and the Ir-substituted compound displayed in Fig. 4(b) have been normalized to their respective values at $\rho(270\,K)$. For clarity, the $\rho(T)$ curves have been shifted vertically relative to the parent compound (black curve) so that the curves are evenly spaced at 270 K by a constant value of $\delta \rho = 0.25$. The temperature dependence of the electrical resistivity is qualitatively similar in both the URu$_{2-x}$Co$_x$Si$_2$ and URu$_{2-x}$Ir$_x$Si$_2$ systems. At high temperatures above 100 K, there is a slight negative temperature coefficient $(d\rho/dT < 0)$; the slight increase in the electrical resistivity as the temperature is reduced is consistent with the scattering from an incoherent single-ion Kondo lattice of atomic U spins. As the temperature is reduced below 50 K in the paramagnetic state, the rapid decrease in $\rho$ suggests the “freezing out” of the spin disorder (or disappearance of U spins) associated with the onset of lattice coherence. The peak in the resistivity curve before the downturn appears to shift to higher temperatures with increasing concentration in both the Co- and Ir-substituted systems. The shift in the lattice coherence to higher temperatures suggests that the introduction of substituent elements Co and Ir fosters mixing of conduction electrons with the $f$ electrons at the uranium site leading to a reduction in the spin disorder across the U sub-lattice. As discussed above, this mixing of the $d$- and $s$-electron bands with the $f$ electrons of the U atoms is also a potential cause for the disruption of the HO phase at lower temperature.

Superconducting transitions at various concentrations $x$ for the URu$_{2-x}M_xSi_2$ $(M = \text{Co, Ir})$ systems are shown in the electrical resistivity data presented in Fig. 4(c). For the Co-substituted compound, the superconductivity is rapidly suppressed as the concentration of Co is increased. The superconducting transition in the parent compound URu$_2$Si$_2$ has a narrow width and a superconducting transition temperature $T_{SC} = 1.5$ K, which is defined as the temperature at which the electrical resistivity is 50% of its value at the onset of the superconducting transition. At a small concentration of cobalt, $x = 0.01$, the superconducting transition temperature has slightly increased to $T_{SC} = 1.6$ K while the superconducting offset temperature $T_{offset}$ has remained the same. However, the width of the transition has noticeably broadened due to an increase in the superconducting onset temperature.

FIG. 3: Dimensions of the unit cell plotted as a function of $x$ for the Co and Ir-substituted systems (a) The lattice parameter $a$ vs $x$ (b) The lattice parameter ratio $c/a$ vs $x$ (c) The lattice parameter ratio $c/a$ vs $x$ (d) The unit cell volume $V = ca^2$ vs $x$. The solid lines are linear fits to the data for the Co-substituted and Ir-substituted systems from $0 \leq x \leq 0.1$ and error bars are shown for the Co- and Ir-substituted systems only. These values are compared with the results from previous studies (dashed lines) for $M = \text{Rh, P and Fe}$. For clarity, the $x = 0$ value was set to be equivalent for all substitutions, $M$. 

[Image 339x538 to 540x790]
from $T_{\text{onset}} = 1.6$ K at $x = 0$ to $T_{\text{onset}} = 1.8$ K at $x = 0.01$. The superconducting onset temperature was determined from the intersection of linear extrapolations (dashed black lines) of the $\rho(t)$ data at the superconducting transition as shown in Fig. 4(c). As the cobalt concentration is increased slightly to $x = 0.02$, the superconductivity is suppressed such that $T_{\text{onset}} = 1.2$ K. At $x = 0.04$, there is no further reduction in the onset of superconductivity when compared to the $x = 0.02$ sample. The full superconducting transitions for $x \geq 0.02$ are not visible due to a limitation of the experimental apparatus in reaching temperatures below 1 K during the measurement.

The suppression of superconductivity in the Co-substituted system with increasing $x$ occurs more slowly when compared to the suppression of superconductivity in the Co-substituted system. The superconducting transition temperature has been reduced slightly from $T_{\text{SC}} = 1.5$ K for the parent compound to $T_{\text{SC}} = 1.4$ K at $x = 0.03$; however, the width of the transition has broadened due to the increase in the superconducting onset temperature from $T_{\text{onset}} = 1.6$ to 1.8 K. As the concentration of Ir is increased further to $x = 0.05$, the superconductivity is suppressed as observed in the reduction of the superconducting onset temperature to $T_{\text{onset}} = 1.2$ K. However, the full superconducting transition was not observed due to a limitation of the experimental apparatus in reaching temperatures below 1 K.

Figure 5 displays the electrical resistivity $\rho(T)$ in the vicinity of the hidden order transition for both the Co- and Ir-substituted URu$_{2-x}$Ir$_x$Si$_2$ compounds. At each concentration, the $\rho(T)$ data displayed in Fig. 5(a) and Fig. 5(b) has been normalized to its respective value at 270 K and the curves have been offset vertically by a constant value of $\delta \rho = 0.1$ for clarity. In this report, the transition temperature $T_{\text{HO}}$ at the PM to HO phase transition is defined to be the temperature at the inflection point in the characteristic spin-density wave-like feature in the electrical resistivity $\rho(T)$. The inflection point in $\rho(T)$ was determined from the minimum in the derivative of the electrical resistivity, $d\rho/dT$ as shown in Fig. 5(c) and Fig. 5(d) for the Co- and Ir-substituted compounds, respectively. Note that there is both a broadening and a decrease in the depth of the minimum in $d\rho/dT$ for both the URu$_{2-x}$Co$_x$Si$_2$ and URu$_{2-x}$Ir$_x$Si$_2$ systems, which indicates the progressive softening of the spin-density wave-like feature in the $\rho(T)$ with increasing Co (or Ir) concentration. The feature becomes vanishingly small such that the HO transition is not observable in $\rho(T)$ by $x = 0.04$ for Ir and $x = 0.05$ for Co. In the case of the Co-substituted compound, the minimum in $d\rho/dT$ is $T_{\text{HO}} = 17.5$ K for both the parent compound and at $x = 0.01$ and then decreases monotonically with a further increase in Co concentration to $T_{\text{HO}} = 14.3$ K at $x = 0.05$. Similarly, for Ir concentrations $x \geq 0.01$, there is a monotonic decrease in $T_{\text{HO}}$ with increasing Ir concentration from $T_{\text{HO}} = 17.5$ K for the parent compound to $T_{\text{HO}} = 15.5$ K for $x = 0.04$.

Extensive experimental work has established the formation of an energy gap $\Delta$ over approximately 40% of the Fermi surface upon the transition to the HO phase in the parent compound URu$_2$Si$_2$. Based on a theoretical model of electrical resistivity (see Eq. (1)), we extracted the magnitude of the energy gap $\Delta$ that forms over a portion of the Fermi surface during the HO phase transition. The exponential term in Eq. (1) represents the contribution to $\rho(T)$ that may occur from the scattering of electrons from spin excitations (or magnons) with a characteristic energy that is gapped at the Fermi energy. For temperatures in the range from just above the superconducting transition temperature $T_{\text{SC}}$ to approximately 10 K, the $\rho(T)$ data is well described by the relatively simple model of electrical resistivity with a quadratic temperature dependence $\rho(T) = \rho_0 + AT^2$ in which the scattering is primarily due to the electron-electron interactions that are characteristic of a Fermi liquid. However, over a larger temperature range that extends from 2 K up to a temperature near the peak in the feature of the electrical resistivity near the HO transition, the fit to the $\rho(T)$ data was improved by using the expression given in Eq. (1).

A summary of the parameters $\rho_0$, $\Delta$, and $B$ as de-
shift to higher temperatures with increasing concentration in both the Co- and Ir-substituted systems.

\[
\rho(T) = \rho_0 + AT^2 + \frac{B}{\Delta^2} \sqrt{\frac{T}{\Delta}} \left[ 1 + 2T^2 + \frac{2}{15} (\frac{T}{\Delta})^2 \right] e^{-\Delta/T} \tag{1}
\]

FIG. 5: The normalized electrical resistivity \( \rho(T)/\rho(270) \), is shown for the \( \text{URu}_{2-x}\text{Co}_x\text{Si}_2 \) (a) and \( \text{URu}_{2-x}\text{Ir}_x\text{Si}_2 \) (b) systems. The \( \rho(T) \) curves were shifted vertically by \( \delta \rho = 0.1 \) for \( M = \text{Co} \) and Ir. The black dashed lines represent fits of the expression for electrical resistivity to the \( \rho(T) \) data and are extrapolated to 17 K. The temperature derivative of the electrical resistivity \( d\rho/dT \) is shown for (c) \( M = \text{Co} \) and (d) \( M = \text{Ir} \). The hidden order transition temperature \( T_{\text{HO}} \) for each sample was determined from the minimum in the \( d\rho/dT \) vs \( T \) curve. The depth of the minimum in \( d\rho/dT \) rapidly decreases with increasing \( x \).

determined from the \( \rho(T) \) data for the \( \text{URu}_{2-x}\text{Co}_x\text{Si}_2 \) and \( \text{URu}_{2-x}\text{Ir}_x\text{Si}_2 \) systems are displayed in Fig. 6 for comparison. The value of \( \rho_0 \) increases slowly with \( x \) which is likely due to increased scattering from the disorder associated with slightly higher levels of substituent elements at the Ru site. (The parameter \( A \) is not shown as it does not vary significantly for the concentrations up to \( x = 0.10 \) reported herein.) The gap amplitude coefficient \( B \) displayed in Fig. 6(b) and the energy gap \( \Delta \) shown in Fig. 6(c) both decrease with increasing \( x \); the uncertainty in the value of \( \Delta \) extracted from the fits to the \( \rho(T) \) data increases significantly with \( x \) owing to the vanishing of the characteristic feature in \( \rho(T) \). Note that the \( B \) and \( \Delta \) parameters were determined only up to \( x = 0.04 \) owing to the vanishing feature in the electrical resistivity associated with the HO transition. Figure 6(d) displays the \( x \) dependence of the temperature of the peak in the electrical resistivity \( T_{\text{coh}} \). The temperature of the peak in the resistivity curve before the downturn appears to shift to higher temperatures with increasing concentration in both the Co- and Ir-substituted systems. The peak at the temperature is consistent with the scattering from an incoherent single-ion Kondo lattice of atomic U spins. As the temperature is reduced in the paramagnetic state below 50 K, the rapid decrease in \( \rho \) suggests the “freezing out” of the spin disorder (or disappearance of U spins) associated with the onset of lattice coherence. The peak in the resistivity curve before the downturn appears to

FIG. 6: The parameters \( \rho(0) \), \( \Delta \), and \( B \) from Eq. 1 are plotted as a function of \( x \) for both the \( \text{URu}_{2-x}\text{Co}_x\text{Si}_2 \) and \( \text{URu}_{2-x}\text{Ir}_x\text{Si}_2 \) systems for \( x \leq 0.04 \). The parameters were determined from fitting Eq. 1 to the \( \rho(T) \) data as described in the text. (a) The normalized residual electrical resistivity \( \rho_0 \) is shown for \( M = \text{Co} \) and Ir; the solid lines are guides to the eye. (b) The energy gap \( \Delta \) plotted as a function of \( x \); the solid lines are guides to the eye. (c) The parameter \( B(x)/B(0) \) vs \( x \); the solid lines are guides to the eye.

C. Specific Heat

Measurements of specific heat \( C(T) \) were performed from 1.8 to 270 K on polycrystalline samples of various concentrations of Co up to \( x = 0.1 \) for the \( \text{URu}_{2-x}\text{Co}_x\text{Si}_2 \) system and similarly for various concentrations of Ir up to \( x = 0.1 \) for the \( \text{URu}_{2-x}\text{Ir}_x\text{Si}_2 \) system. Specific heat data in the vicinity of the HO transition temperature \( T_{\text{HO}} \) are shown in Fig. 7a for the \( \text{URu}_{2-x}\text{Co}_x\text{Si}_2 \) system for \( x \leq 0.06 \). A similar presentation of \( C(T) \) data for the Ir-substituted compound is shown in Fig. 7b. The second-order mean-field BCS-like feature in the specific heat is a signature of the transition from the paramagnetic phase to the HO phase at \( T_{\text{HO}} = 17.5 \) K during which there is a partial gapping over approximately 40% of the Fermi surface, and an associated loss in entropy for the parent compound \( \text{URu}_2\text{Si}_2 \).
For both the Co- and Ir-substituted compounds, the magnitude of the feature diminishes in height and broadens in width as the concentration $x$ is increased; the feature becomes unobservable at $x = 0.10$ suggesting the vanishing of the charge gap. The reduction of the size of the jump in the specific heat at the HO transition temperature $T_{\text{HO}}$ is consistent with a scenario in which there is a "gapless" HO phase.

In order to emphasize the evolution of the HO transition temperature $T_{\text{HO}}$ with increasing $x$, the temperature derivative of the specific heat $dC/dT$, is shown in Fig. 7c and Fig. 7(d) for the URu$_{2-x}$Co$_x$Si$_2$ and URu$_{2-x}$Ir$_x$Si$_2$ systems, respectively. The temperature at which there is a minimum in $dC/dT$ is defined to be the HO transition temperature $T_{\text{HO}}$. There is a consistent decrease of $T_{\text{HO}}$ for the URu$_{2-x}$Co$_x$Si$_2$ system while there is a slight decrease in $T_{\text{HO}}$ for the URu$_{2-x}$Ir$_x$Si$_2$ system. The values of $T_{\text{HO}}$ as determined from the specific heat $C(T)$ measurements are presented graphically in the $T-x$ phase diagram displayed in Fig. 11 in the Discussion section below.

Displayed in Fig. 8(a) is the electronic contribution to the specific heat divided by temperature $C_e(T)/T$, plotted as a function of $T$ for the URu$_{2-x}$Co$_x$Si$_2$ system at the concentration $x = 0.02$. For each concentration $x$, in both the URu$_{2-x}$Co$_x$Si$_2$ and URu$_{2-x}$Ir$_x$Si$_2$ systems, we performed a fit of the expression $C/T = \gamma + \beta T^2$ to the measured specific heat $C(T)/T$ in a small four-degree window of temperature just above $T_{\text{HO}}$. This allowed us to determine the electronic component of the specific heat $C_e(T)/T$ by subtracting the lattice contribution $\beta T^2$ from the measured specific heat $C(T)/T$. The solid red line is the subtracted specific heat data (or electronic component of the specific heat, $C_e(T)/T$) and the black dashed line is a fit of the expression $C_e(T)/T = \gamma + \alpha e^{-\Delta/k_B T}$ to the subtracted specific heat data, $C_e(T)/T$. The $y$-intercepts of the purple and blue dashed lines yield the values of $\gamma_0$ and $\gamma_1$, respectively. The values for $\gamma_0$ and $\gamma_1$ are shown in Fig. 8(b) for both the Co- and Ir-substituted compounds as a function of $x$ up to $x = 0.08$. For small increases in $x$ up to 0.04 in both the URu$_{2-x}$Co$_x$Si$_2$ and URu$_{2-x}$Ir$_x$Si$_2$ systems, $\gamma_1$ tends to decrease while $\gamma_0$ tends to increase. In the absence of any BCS-like feature associated with the HO phase transition, it is expected that $\gamma_0$ should be equal to $\gamma_1$, which is indeed observed at a high concentration of Co ($x = 0.08$), where there is scarce evidence of the HO phase transition in the measured specific heat $C(T)$.

The Debye temperature $\Theta_D$ and $\gamma_1$ were determined by fitting a straight line though $C/T$ vs $T^2$ in the region above the HO. In this temperature window, there is not a significant HO gap contribution and $C(T)$ is well described by the Debye model. In Fig. 8(c) we show $\Theta_D$ for $M = \text{Co}$ and $\text{Ir}$; only the Co-substituted system exhibits a modest increase in $\Theta_D$ with $x$.

The low-temperature portion of the anomalous BCS-like feature in the specific heat $C(T)$ is described by the exponential term shown in Eq. 2, which is sensitive to the magnitude of the energy gap $\Delta$. The magnitude of the energy gap $\Delta$ was found by subtracting $\beta T^2$ from $C(T)/T$ in Eq. 2 and then fitting the exponential function to the subtracted data as described in the previous paragraph. In Fig. 8(d), $\Delta$ vs $x$ is shown for the URu$_{2-x}$Co$_x$Si$_2$ and URu$_{2-x}$Ir$_x$Si$_2$ systems and both exhibit a similar decrease in $\Delta$ with $x$. Initially, $\Delta$ varies linearly with $x$. However, for $x \geq 0.04$, the curvature changes and we used fits to second order polynomials to guide the eye. It should be noted that for $x \geq 0.04$, the accuracy of measuring $\Delta$ decreases significantly due to the diminishing amplitude of the feature in $C(T)$. The amplitude or size of the jump in the electronic specific heat $\delta C_e$, plotted as a function of $x$, is displayed in Fig. 8(d). For small increases in $x$, the rapid suppression of $\delta C_e$ at the transition temperature $T_{\text{HO}}$ in both systems suggests there may be an emergent HO phase with no energy gap $\Delta$.

Displayed in Fig. 9(a) and (b) we show the electronic contribution to the specific heat, $C_e/T$, for the Co- and Ir-substituted samples, respectively. The value of $C/T$

![Diagram](image-url)
at the flat region before the onset of the HO phase is defined as $\gamma_0$ based on the procedure described above and illustrated in Fig. 8(a). For both the URu$_{2-x}$Co$_x$Si$_2$ and URu$_{2-x}$Ir$_x$Si$_2$ systems, the peak in the electronic specific heat $C_e/T$ is rapidly reduced with increasing $x$ and nearly flat at $x = 0.06$; at lower temperature in the HO phase below $T_{HO}$, there is an increase in the minimum value in $C_e/T$ at approximately 8 K as indicated by the left arrow. The evolution of $T_{HO}$ with $x$ is illustrated with the arrow on the right.

To calculate the electronic component of the entropy $S_e$, the electronic specific heat $C_e/T$ was extrapolated to zero in a similar manner in the determination of $\gamma_0$ in Fig. 8 and then the entropy was determined from the integral $\int_0^T \frac{C_e}{T} dT$. The electronic contribution to the entropy is displayed in Fig. 9(c) and (d) for the URu$_{2-x}$Co$_x$Si$_2$ and URu$_{2-x}$Ir$_x$Si$_2$ systems, respectively. It is suggested that the electronic ordering and the associated partial (40%) gapping of the Fermi-surface upon the HO phase transition results in a reduction of the entropy.\textsuperscript{15,17} However, as displayed in Fig. 9(c) and (d), an increase in the concentration $x$ results in a decrease in both the height of the feature in the specific heat and also the energy gap $\Delta$ (see Fig. 8(d)); the result is a smaller reduction in the entropy. For concentrations of $x \geq 0.06$, the feature in the electronic component of the entropy is non-existent. For URu$_{0.97}$Ir$_{0.03}$Si$_2$, the specific heat $C(T)$ data was not measured below 10 K; consequently, $S_e$ is not displayed for this concentration.

**D. DC Magnetization**

The results for $M(T)/H$ over the entire range in temperature from 270 to 1 K are shown in Fig. 10 (a) for several concentrations of $M = Co$ and Ir. The $M(T)/H$ curves have been offset vertically by $\delta M = 1.0$ (emu/mol.Oe) for visual clarity. The coherence peak can be seen in the rounded maximum in the $M(T)/H$ data at $T_{coh} \approx 60$ K which signals the onset of the coherence in the heavy-fermion state that precedes the transition to HO at $T_{HO} = 17.5$ K. This is consistent with a similar maximum observed in the $\rho(T)$ which is near 75 K. As $x$ is increased in both the Co- and Ir-substituted systems, there was a slight increase observed in the temperature of the peak in the electrical resistivity $T_{coh}$. In contrast, the change in $T_{coh}$ with increasing $x$ from $x = 0$ to $x = 0.1$ was insignificant in the $M(T)/H$ data. At low temperature, the upturns in the $M(T)/H$ data for several of the $M = Co$ samples are possibly due to the presence of trace ferromagnetic impurities, or a consequence of the greater
disorder in the Co-substituted samples.

In Fig. 10(b), the inverse magnetization \((H/M)\) as a function of temperature is displayed for the parent compound URu\(_2\)Si\(_2\) and for the URu\(_2-x\)Ir\(_x\)Si\(_2\) \(M = \text{Co and Ir}\) systems at several concentrations of Co with \(x = 0.01, 0.05, \) and 0.1 and Ir with \(x = 0.05, 0.06.\) Again, the \(H/M(T)\) data have been offset by \(\delta_{H/M} = 0.1\) (mol.Oe/emu) for clarity. The dashed black lines show the linearity of the \(H/M\) vs \(T\) data in the paramagnetic phase over the temperature range \(150 \leq T \leq 270.\) The Curie-Weiss relation \(H/M = C_0/(T - \Theta_{CW})\) was applied to determine the Curie-Weiss temperature \(\Theta_{CW}\) and the effective moment \(\mu_{eff}.\) For higher concentrations, \(\Theta_{CW}\) and \(\mu_{eff}\) both decrease,\(^7\) whereas \(\Theta_{CW}\) and \(\mu_{eff}\) were nearly constant for \(x \leq 0.1\) indicating that there is not a significant effect on the high temperature paramagnetic properties for low concentrations of \(M = \text{Co, Ir}..\)

In Fig. 10(c), the \(M(T)/H\) data is shown for URu\(_2\)Si\(_2\) to the \(x = 0.04\) Co and \(x = 0.05\) Ir samples. For \(x \geq 0.03\) the transition observed in \(M(T)\) becomes merely a “kink”. The feature in the magnetization is substantially reduced relative to the parent compound for URu\(_{1.96}\)Co\(_{0.04}\)Si\(_2\) and URu\(_{1.95}\)Ir\(_{0.05}\)Si\(_2\). The hidden order transition temperature \(T_{HO}\) may be estimated from a graphical construction highlighting the change in slope which is shown by the dashed line in Fig. 10(c). The quantitative accuracy of determining \(T_{HO}\) from the magnetization is considerably less than from \(C(T)\) or \(\rho(T)\), due to the lack of an inflection point. It is worth mentioning that our previous report from 1989,\(^3\) for the evolution of \(T_{HO}\) in URu\(_{2-x}\)Ir\(_x\)Si\(_2\), was primarily based on a single magnetization measurement at \(x = 0.05\), which also had a large margin of error for estimating \(T_{HO}.\) Consequently, the phase diagram constructed from the specific heat measurements of this study supersede our previous work.

**IV. DISCUSSION**

The measurements of electrical resistivity \(\rho(T)\) and specific heat \(C(T)\) were used to construct \(T-x\) phase diagrams for both the URu\(_{2-x}\)Co\(_x\)Si\(_2\) and URu\(_{2-x}\)Ir\(_x\)Si\(_2\) systems and are presented in Fig. 11(a) and Fig. 11(b), respectively. The hidden order transition temperature \(T_{HO}\) for the Co-substituted system decreases monotonically and nearly linearly with \(x\) while \(T_{HO}\) for the Ir-substituted system initially decreases with \(x\) and then remains unchanged for \(x > 0.03.\) As mentioned previously, the feature in both the \(\rho(T)\) and \(C(T)\) data which marks the HO transition is greatly diminished even at low concentrations of both Co and Ir, such that by \(x = 0.1\), there is no measurable HO transition in the electrical resistivity \(\rho(T)\) or specific heat \(C(T)\) measurements for either the URu\(_{2-x}\)Co\(_x\)Si\(_2\) or URu\(_{2-x}\)Ir\(_x\)Si\(_2\) system. However, up to \(x = 0.1\) in each system, the determination of \(T_{HO}\) from \(\rho(T)\) are in good agreement with that of the \(C(T)\) data. (We mention that the feature at the HO transition in the \(C(T)\) data is more pronounced and hence there is less uncertainty in the determination of the magnitude of the energy gap \(\Delta\) from the fitting procedure.)

The suppression of superconductivity tracks the suppression of hidden order at roughly the same rate as can be seen from a comparison of the \(T_{onset}(x)\) and \(T_{HO}(x)\) phase boundaries up to \(x = 0.06\) in both Fig. 11(a) and Fig. 11(b). The temperature for the onset of superconductivity \(T_{onset}\), as determined from the electrical resistivity measurements, is suppressed with increasing \(x\) for both the URu\(_{2-x}\)Co\(_x\)Si\(_2\) and URu\(_{2-x}\)Ir\(_x\)Si\(_2\) systems as shown in Fig. 11(a) and Fig. 11(b), respectively. However, the suppression of \(T_{onset}\) is initially stronger for the case of the Co-substituted system as seen in the positive curvature in the \(T_{onset}\) vs \(x\) phase boundary in Fig. 11(a) compared to the nearly linear suppression in the Ir-substituted system displayed in Fig. 11(b). The onset temperature \(T_{onset}\) is visible in the \(\rho(T)\) data up to \(x = 0.06;\) at higher concentrations, the onset of super-
conductivity is no longer observable during the electrical resistivity measurement due to the onset temperature $T_{\text{onset}}$ being lower than the temperature limit ($\sim 1.1$ K) imposed by the cryostat apparatus.

In the limit of small concentrations of $M = \text{Co}$ and Ir in the two URu$_{2-x}M_x\text{Si}_2$ systems, the suppression of HO may be explained by the expression in Eq. 3, which gives the HO transition temperature $T_{\text{HO}}$ as a function of concentration $x$:

$$T_{\text{HO}}(x) = \frac{\Delta_0 + x\Delta_1}{2 \text{arctanh}((\Delta_0 + x\Delta_1)/J^\psi)}. \quad (3)$$

Here, the values of $\Delta_0 = 35$ K and $J^\psi = 46.24$ K were taken from Ref. 19. At the critical concentration $x_c$, where the HO transition temperature $T_{\text{HO}} = 0$ K, the expression in Eq. 3 can be written as $\Delta_0 + x_c\Delta_1 = J^\psi$. This requires a determination of the critical concentration $x_c$. The critical concentrations of $x_c = 0.11$ for the URu$_{2-x}\text{Co}_x\text{Si}_2$ system and $x_c = 0.10$ for the URu$_{2-x}\text{Ir}_x\text{Si}_2$ system were determined by a similar procedure as reported in Ref. 19 by linearly extrapolating the $\Delta(x)$ curve to zero K as shown in Fig. (8d). The dashed purple line in both Fig. 11 (a) and (b) represents the $x$ dependence for $T_{\text{HO}}$ as determined from the expression in Eq. 3.19 The model predicts a linear decrease in $T_{\text{HO}}$ for low $x$ in which the paramagnetic phase is stable against the formation of the HO phase owing to the impurity-induced strain and increase in the crystal field parameter.19 The linear decrease in $T_{\text{HO}}$ for low values of $x$, successfully describes the decrease in $T_{\text{HO}}$ for the Co-substituted compound up to $x = 0.08$; however, for samples from the Ir-substituted system, the evolution of the phase boundary $T_{\text{HO}}(x)$ diverges relatively quickly from the $T_{\text{HO}}(x)$ curve determined from Eq. 3. This suggests the paramagnetic phase in the Ir-substituted URu$_2\text{Si}_2$ compound is less stable to the formation of the HO phase (or a possible parasitic antiferromagnetic phase at higher concentrations and lower temperatures). Due to the vanishing signature of the HO transition at $x = 0.05$ in measurements of both $\rho(T)$ and $C(T)$, we did not determine $T_{\text{HO}}$ in the region of concentration ($x \geq 0.10$) where the model rapidly decreases with $x$.

Based on our measurements of x-ray diffraction and electrical resistivity, the introduction of small amounts of $M = (\text{Co}, \text{Ir})$ results in a minimal increase in the intrinsic disorder in the compound. Substitution of $M = \text{Co}$ and Ir for Ru in the URu$_{2-x}M_x\text{Si}_2$ systems likely introduces additional conduction electrons in the Ru-Si layer, although this has no significant effect on the absolute electrical resistivity. Furthermore, although the change in the lattice constants are proportional to $x$, any chemical pressure effects are small at these concentrations which are well below the level at which the characteristic features of the HO phase transition have vanished in both the electrical resistivity and specific heat. However, as Ru atoms are replaced with $M = \text{Co}, \text{Ir}$, there is likely to be a change in the interactions between the $d$ electrons of the Ru atoms and the $f$ electrons of the U atoms. There are many examples of strongly correlated intermetallic compounds that do not order magnetically owing to the strong hybridization of the conduction electrons with the $5f$ electrons of the U atoms. An increase in this type of interaction between the $d$ electrons of the $M = (\text{Co}, \text{Ir})$ atoms and the $f$ electrons of the U atoms might play a role in disrupting the formation of the HO state. Indeed, it has been shown that the substitution of Ge (germanium) for Si (silicon) does not directly influence the wavefunction overlap between the $5f$ electrons of the U atom and the $d$ electrons in the intermetallic band and has a minimal effect on the hidden order transition temperature $T_{\text{HO}}$ and charge gap $\Delta$ up to 30% concentration ($x = 0.6$ in URu$_{2-x}\text{Ge}_x\text{Si}_2$). The rapid attenuation of the HO state upon chemical substitution...
FIG. 12: (a) Energy gap $\Delta$, determined from the specific heat $C(T)$, is shown as a function of the HO transition temperature $T_{\text{HO}}$ for $0 \leq x \leq 0.09$ for URu$_{2-x}$Co$_x$Si$_2$ (open circles) and URu$_{2-x}$Ir$_x$Si$_2$ (red squares). The solid red and black lines are linear fits to the $T_{\text{HO}}$ values determined from the specific heat $C(T)$. The dashed blue line represents the behavior of $\Delta$ for a scenario in which the HO phase remains gapped down to $T_{\text{HO}} = 0$ K as is consistent with the BCS law of corresponding states. (b) $\Delta/T_{\text{HO}}$ vs $T_{\text{HO}}$ with the dashed blue horizontal line representing the behavior consistent with the BCS law of corresponding states. (c) $\delta C_e/T_{\text{HO}}$ vs $T_{\text{HO}}$ is shown with the dashed blue horizontal line representing the behavior consistent with the BCS law of corresponding states.

was found that the relatively moderate rate of suppression of $T_{\text{HO}}$ is smaller than the rate at which the charge gap $\Delta$ is suppressed, leading to a hidden order phase with a Fermi surface that is no longer gapped. In this report, we observed comparable rates of suppression in both the Co- and Ir-substituted systems, suggesting a similar scenario in which the compound enters a “gapless” HO phase before it becomes superconducting upon further cooling. Figure 12 presents a comparison of the rates of suppression for the charge gap $\Delta$ and the HO transition temperature $T_{\text{HO}}$ for both the Co- and Ir-substituted systems. The blue dashed line in Fig. 12(a) represents the evolution of a conventionally gapped HO phase that is suppressed to zero K in proportion to the suppression of the charge gap $\Delta$ according to the BCS (Bardeen-Cooper-Schrieffer) law of corresponding states. In the case of a second-order, mean-field transition as described in the weak coupling regime of the BCS theory of conventional superconductivity, both the energy gap $\Delta$ and the magnitude of the jump in the electronic specific heat $\delta C$ scale with the superconducting transition temperature $T_{\text{SC}}$ such that the ratio of the energy gap to the superconducting transition temperature $\Delta/T_{\text{SC}}$ remains constant at 1.76, even as $T_{\text{SC}}$ is reduced. The red ($M = \text{Ir}$) and black ($M = \text{Co}$) solid lines are linear fits to the data and indicate clear deviations from the BCS law of corresponding rates in which $\Delta$ is reduced to zero K before $T_{\text{HO}}$ is suppressed to zero K.

An alternative representation of the deviation from the BCS law of corresponding states is displayed in Fig. 12(b), in which the ratio of the charge gap to the HO transition temperature, $\Delta/T_{\text{HO}}$, is shown to decrease by a factor of roughly three over the range of data from $T_{\text{HO}} = 17.5$ K down to $T_{\text{HO}} = 14$ and 16 K for the URu$_{2-x}$Co$_x$Si$_2$ and URu$_{2-x}$Ir$_x$Si$_2$ systems, respectively. Again, the dashed blue line is the constant ratio expected for a conventionally gapped system according to the BCS law. Figure 12(c) illustrates the deviation from the BCS law in the ratio of magnitude of the jump in the electronic specific heat $\delta C$ to the HO transition temperature $T_{\text{HO}}$. The BCS law of corresponding states predicts a constant ratio $\delta C/T_{\text{HO}}$ as the transition temperature progresses to lower temperature, which is clearly not represented here as seen in the discrepancy between the dashed blue line and the solid red and black lines. For URu$_2$Si$_2$ systems that do not transition into a large moment antiferromagnetic phase, i.e., the iso-electronic substitutions of Fe and Os for Ru in the URu$_{2-x}$Fe$_x$Si$_2$ and URu$_{2-x}$Os$_x$Si$_2$ systems, this type of behavior in which $\Delta$ and $\delta C$ are rapidly suppressed below the BCS law appears to be universal for systems involving both electronic and hole doping at the U, Ru, and Si atomic sites.\(^{7,18,22,23}\)

of Co and Ir for the Ru atom supports the idea that the HO phase depends strongly on electronic tuning outside of the $f$-electron shells of the uranium atoms. This is also the case in the P (phosphorous) substituted system in which the hidden order phase appears to strongly depend on electronic tuning external to the $f$-electron shells.\(^{18}\)

Figure 11(c) displays the initial $T_{\text{HO}}$ vs $x$ behavior up to $x = 0.08$ for several URu$_{2-x}$M$_x$Si$_2$ systems with various transition metals $M = \text{Fe}^{10}$, Ir, Re$^5$, Co, and Rh$^5$ substituted for Ru. It is clear that the rate of suppression of the HO phase is not the same for each of the substituent elements $M$; the rate of suppression is largest for the Rh-substituted system while the Fe-substituted system is nearly independent of $x$ in this concentration range. We note that, except in the case of the Fe-substituted system, the feature in the $\rho(T)$ and $C(T)$ data at the HO transition for each of these systems is not observable for their respective substituent concentrations above $x = 0.2$.

In a recent report on the URu$_{2-x}$Re$_x$Si$_2$ system,\(^{21}\) it
V. CONCLUSION

The systematic study of the effects of elemental substitution at the Ru site in URu$_2$Si$_2$ reveal that the HO transition temperature $T_{\text{HO}}$ is rapidly suppressed with modest increases in concentration for those elements in adjacent columns to the left ($M = \text{Mn, Tc, Re}$) and right ($M = \text{Co, Rh, Ir}$) of the column in the periodic table containing Ru. Our results for the substitution of $M = \text{Co, Ir}$ for Ru in URu$_{2-x}M_x$Si$_2$ are consistent with the suppression of HO in the Rh-substituted system, although the rates of suppression are less in the case of URu$_{2-x}$Co$_x$Si$_2$ and significantly less in the case of URu$_{2-x}$Ir$_x$Si$_2$. We also observed an accelerated suppression of the charge gap $\Delta$ in both the URu$_{2-x}$Co$_x$Si$_2$ and URu$_{2-x}$Ir$_x$Si$_2$ systems that is inconsistent with the BCS law of corresponding states. In contrast to the BCS law, which predicts that the charge gap $\Delta$ should scale with the suppression of the transition temperature $T_{\text{HO}}$, we observed a threefold reduction in the BCS ratio $\Delta/T_{\text{HO}}$ down to $T_{\text{HO}} = 14$ and 16 K for the URu$_{2-x}$Co$_x$Si$_2$ and URu$_{2-x}$Ir$_x$Si$_2$ systems, respectively; in both of these systems, an extrapolation of the $\Delta$ vs $T_{\text{HO}}$ curve to zero K reveals the existence of an HO phase that is gapless at $T_{\text{HO}} \approx 15$ K. These results are consistent with a recent report of a “gaples” HO phase at $T_{\text{HO}} = 10$ K in URu$_{2-x}$Re$_x$Si$_2$. This decrease in the BCS ratio $\Delta/T_{\text{HO}}$ appears to be nearly universal for other URu$_2$Si$_2$-based systems including systems with substitutions on the U and Si sites in addition to the Ru site. It is interesting to note that in the case of the isoelectronic substitution of $M = \text{Fe or Os}$, $T_{\text{HO}}$ is nearly independent of small increases in the substituent concentration of Fe while in the case of $M = \text{Os}$, there is a slight enhancement of $T_{\text{HO}}$ with small increases in the Os concentration. These two isoelectronic substitutions result in an overall enhancement of the charge gap $\Delta$ in the URu$_{2-x}$Fe$_x$Si$_2$ and URu$_{2-x}$Os$_x$Si$_2$ systems. In contrast to nearly every other URu$_2$Si$_2$-based system, these two systems are unique in that they exhibit a first order transition to an antiferromagnetic phase similar to the pressure-induced phase transition observed in the parent compound URu$_2$Si$_2$.

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