Effect of transition-metal substitutions on competing electronic transitions in the heavy-electron compound URu_2Si_2

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The moderately heavy-electron compound URu_2Si_2 is known to exhibit two electronic phase transitions at low temperatures, one to an antiferromagnetically ordered state at $T_N = 17.5$ K followed by another to a superconducting state at $T_c \sim 1.5$ K. The shape of the specific-heat anomaly at T_N , which is reminiscent of a second-order BCS-type mean-field transition, suggests the formation of a spin- or charge-density wave opening a gap over part of the Fermi surface. The effect of chemical substitution of the transition metals $M = \text{Re, Tc, Os, Rh, and Ir}$ for Ru in URu_2Si_2 has been investigated by means of electrical resistivity, magnetic susceptibility, and specific-heat measurements in $\text{URu}_{2-x}\text{M}_x\text{Si}_2$ for $x \leq 0.2$. The anomaly associated with the 17.5 K transition involves a very small magnetic entropy and is smeared out by very small concentrations of the M substituent. An inverse correlation between T_c and T_N in the Rh- and Ir-doped materials for $x < 0.01$ and in the Os-doped series for $x < 0.1$ is consistent with the picture of two electronic transitions competing for states at the Fermi level.

INTRODUCTION

Heavy-electron rare-earth and actinide compounds have been of enormous interest over the past decade because of their remarkable normal- and superconducting-state properties.¹ At high temperatures (typically, $T \gtrsim 100$ K), the compounds exhibit localized f -electron behavior and the electrical resistivity is large, of the order of $100 \mu\Omega \text{ cm}$, whereas at low temperatures, the moments appear to be screened by the conduction electrons and the materials behave as strongly interacting Fermi liquids in which the quasiparticles (so-called heavy electrons) can be pictured as a superposition of localized f electrons and conduction electrons. These quasiparticles have an effective mass m^* , inferred from the coefficient γ of the electronic contribution to the specific heat, as high as several hundred times the free-electron mass. Some of these materials (e.g., CeCu_2Si_2 , UBe_{13} , UPt_3 , and URu_2Si_2) exhibit superconductivity below 1.5 K, characterized by power-law dependences in the superconducting

properties that are consistent with zeroes in the energy gap at points or lines on the Fermi surface.

Of this rich class of materials, the moderately heavy-electron compound URu_2Si_2 ($m^* \approx 25m_e$) (Ref. 2–4) and, as recently reported, the heavy-electron compounds UPt_3 (Ref. 5) and $\text{CeCu}_{2.1}\text{Si}_2$ (Ref. 6) show the coexistence of magnetism and superconductivity. The interplay between these two phenomena has been thoroughly studied in systems such as RRh_4B_4 and RMO_6S_8 , where R = rare earth.⁷ In the latter compounds, magnetism and superconductivity are associated with two different subsets of electrons ($4f$ and $4d$, respectively), whereas in the heavy-electron materials the magnetic and/or superconducting properties are determined by the same electrons ($4f$ for rare earth and $5f$ for actinide compounds). Several heavy-electron compounds such as U_2Zn_{17} , UCd_{11} , and UCu_5 have been found to develop a magnetic ground state associated with the removal of part of the Fermi surface.^{8–10} Alloy systems such as $(\text{U,Th})\text{Pt}_3$ and $\text{U}(\text{Pt,Pd})_3$ are also examples in which doping induces a

long-range spin-density-wave (SDW) state^{11,12} at the expense of superconductivity in UPt_3 . The compound URu_2Si_2 exhibits two distinct electronic transitions: bulk superconductivity below 1.5 K and a second transition at $T_N = 17.5$ K. According to neutron scattering experiments on a URu_2Si_2 single crystal, the phase transition at 17.5 K is due to antiferromagnetic ordering with a very small moment on the U site equal to $0.03 \pm 0.01 \mu_B$ and a modulation along the (1,0,0) direction.¹³ The strongest evidence for a spin- or charge-density wave (SDW or CDW) in URu_2Si_2 comes from specific-heat data. We pointed out⁴ that the anomaly δC associated with the 17.5 K transition has a shape reminiscent of a second-order BCS-type mean-field transition that can be described by the relation $\delta C = A \exp(-\Delta/T)$, where the activation energy $\Delta \approx 11$ meV, and that the electronic-specific-heat coefficient γ is reduced from 112 mJ/mol K² above T_N to 65.5 mJ/mol K² above 1.5 K. These observations along with the Cr-like anomaly in the electrical resistivity and the small change in the magnetic susceptibility near 17.5 K led us to propose the establishment of a spin- or charge-density wave at T_N that opens a gap over $\sim 40\%$ of the Fermi surface. The absence of any structural transition in the vicinity of 17.5 K from x-ray-diffraction measurements that we made at various temperatures between 4 and 300 K suggests that the phase transition at T_N is most likely associated with the establishment of a commensurate¹³ SDW state. Nuclear magnetic resonance,¹⁴ Hall effect¹⁵ and thermoelectric power¹⁶ measurements have been interpreted in favor of a SDW and/or CDW ground state in URu_2Si_2 . Walter *et al.* reported the observation at $T = 10$ K of a 5.5 meV gaplike magnetic excitation in the inelastic neutron scattering spectrum of a URu_2Si_2 polycrystalline sample.¹⁷

The purpose of this work is to obtain information about the competing electronic ground states in URu_2Si_2 by studying the effect of $4d$ and $5d$ transition-metal impurities on its physical properties. Chemical substitution of transition-metal M ions for Ru is a direct way of varying the conduction-electron density and in turn modifying the topology of the Fermi surface, thus affecting the delicate balance between the electronic phase transitions at 1.5 and 17.5 K. We have investigated a number of pseudoternary $\text{URu}_{2-x}M_x\text{Si}_2$ compounds, where $M = \text{Tc, Re, Os, Rh, and Ir}$ for $0 \leq x \leq 0.2$, by means of electrical resistivity ρ , magnetic susceptibility χ , and specific-heat C measurements as functions of temperature T in the range $70 \text{ mK} \leq T \leq 300 \text{ K}$.

EXPERIMENTAL DETAILS

The polycrystalline $\text{URu}_{2-x}M_x\text{Si}_2$ samples were prepared by arc-melting stoichiometric amounts of the constituent elements together on a water-cooled-cooper hearth in a Zr-gettered-ultrapure-argon atmosphere. The constituent elements had the following purities: U 99.9%, Ru 99.9%, Re 99.99%, Rh 99.9%, Os 99.9%, Ir 99.99%, Tc 99.9%, and Si 99.999999%. To control the stoichiometry for low-impurity concentrations ($x < 0.05$),

appropriate amounts of $\text{URu}_{2-\delta}T_\delta\text{Si}_2$ with $\delta \leq 0.3$ and URu_2Si_2 master compounds were combined and melted together. The ingots were melted several times on each side to insure homogeneity, wrapped in Ta foil, sealed in a quartz tube in a 150 torr argon atmosphere, and annealed at 900°C for 8 days. X-ray-diffraction measurements revealed no impurity phases in all samples. Electrical resistivity measurements on bar-shaped specimens were made in a He⁴ cryostat using a four-lead ac impedance bridge operating at 16 Hz. The dc magnetic susceptibility was measured in a field of 5 kOe with a commercial superconducting quantum interference device (SQUID) susceptometer. The ac magnetic susceptibility was measured in a ³He-⁴He dilution refrigerator and the specific-heat data were taken using a semiadiabatic ³He calorimeter with the standard heat-pulse method.

RESULTS

The ternary compounds UM_2Si_2 for $M = \text{Ru, Rh, Os, and Ir}$ crystallize in the body-centered-tetragonal ThCr_2Si_2 structure,¹⁸ while UTc_2Si_2 and URe_2Si_2 form in a body-centered-cubic URu_2Si_2 -type structure.¹⁹ All specimens of the $\text{URu}_{2-x}M_x\text{Si}_2$ series with $M = \text{Tc, Re, Os, Rh, Ir, Os, and } x \leq 0.2$ were found to form in the ThCr_2Si_2 structure. The composition dependence of the lattice parameters was investigated by means of x-ray analysis. The lattice parameters a and c determined by a least-squares fit of the high-angle lines are listed in Table I. Doping seems to decrease a and increase c in most cases except for Os, in which case an initial increase of c is followed by a decrease above $x = 0.02$.

The effect of transition-metal M doping on the temperature dependence of the electrical resistivity ρ of the $\text{URu}_{2-x}M_x\text{Si}_2$ ($M = \text{Rh, Ir, Os, and Re}$) materials has been determined. The results are displayed in Figs. 1 and 2 as plots of the normalized electrical resistivity $\rho/\rho(300 \text{ K})$ versus temperature T . Figure 1 shows representative data for $M = \text{Ir}$ only. Also, for the sake of clarity, data for some values of x are not shown. The three main regimes revealed above 20 K in the $\rho(T)$ data for URu_2Si_2 (Fig. 1) are (1) an increase in ρ , as T is lowered from 300 to ~ 80 K, which is associated with the Kondo scattering of the conduction electrons by independent spins; (2) the development of a broad maximum in $\rho(T)$ centered near $T_M \approx 79$ K; and (3) a rapid decrease in ρ as the temperature is lowered further. This latter feature is associated with the onset of coherent scattering of the conduction electrons by the periodically distributed U ions. Below 20 K, a narrow peak associated with the SDW transition develops in the vicinity of $T_N = 17.5$ K. The value of T_N is defined by the minimum in the $(1/\rho)(d\rho/dT)$ versus T curve as plotted for $\text{URu}_{2-x}\text{Rh}_x\text{Si}_2$ in Fig. 3. Finally, there is a transition to the superconducting state below $T_c \approx 1.5$ K.

The effect of doping on the shape of $\rho(T)$ is minimal above T_M . The temperature coefficient of resistivity remains negative as in URu_2Si_2 but of lower (Ir and Re) or higher (Rh and Os) magnitude than for the pure compound, which is qualitatively consistent with a respective

TABLE I. Lattice parameters for $\text{URu}_{2-x}\text{M}_x\text{Si}_2$ alloys determined from x-ray-diffraction measurements at 300 K.

Compound	$a(\text{\AA})$	$c(\text{\AA})$	c/a	$V(\text{\AA}^3)$
URu_2Si_2	4.142	9.559	2.308	164.00
$\text{URu}_{1.995}\text{Rh}_{0.005}\text{Si}_2$	4.133	9.584	2.319	163.71
$\text{URu}_{1.99}\text{Rh}_{0.01}\text{Si}_2$	4.132	9.598	2.323	163.87
$\text{URu}_{1.98}\text{Rh}_{0.02}\text{Si}_2$	4.125	9.594	2.326	163.25
$\text{URu}_{1.95}\text{Rh}_{0.05}\text{Si}_2$	4.125	9.621	2.332	163.71
$\text{URu}_{1.9}\text{Rh}_{0.1}\text{Si}_2$	4.142	9.624	2.324	165.11
$\text{URu}_{1.99}\text{Os}_{0.01}\text{Si}_2$	4.131	9.577	2.318	163.43
$\text{URu}_{1.98}\text{Os}_{0.02}\text{Si}_2$	4.125	9.594	2.326	163.25
$\text{URu}_{1.97}\text{Os}_{0.03}\text{Si}_2$	4.132	9.574	2.317	163.46
$\text{URu}_{1.95}\text{Os}_{0.05}\text{Si}_2$	4.133	9.567	2.315	163.42
$\text{URu}_{1.9}\text{Os}_{0.1}\text{Si}_2$	4.117	9.544	2.318	161.77
$\text{URu}_{1.99}\text{Ir}_{0.01}\text{Si}_2$	4.132	9.504	2.300	162.27
$\text{URu}_{1.98}\text{Ir}_{0.02}\text{Si}_2$	4.112	9.587	2.331	162.10
$\text{URu}_{1.95}\text{Ir}_{0.05}\text{Si}_2$	4.132	9.618	2.328	164.21
$\text{URu}_{1.9}\text{Re}_{0.1}\text{Si}_2$	4.142	9.550	2.306	163.84
$\text{URu}_{1.8}\text{Re}_{0.2}\text{Si}_2$	4.138	9.583	2.316	164.09
$\text{URu}_{1.88}\text{Tc}_{0.12}\text{Si}_2$	4.134	9.571	2.315	163.57

increase or decrease of the Kondo temperature T_K . The temperature T_M of the maximum in $\rho(T)$ is invariably shifted to higher temperatures as indicated in Table II, except for Rh, where it decreases with increasing x . Below T_M , all $\rho(T)$ curves show coherent scattering of the conduction electrons. The most dramatic effect of the transition-metal substitution is on the phase transition at T_N as shown in Fig. 2. The partial replacement of Ru with nonisoelectronic Ir, Re, or Rh atoms results in a decrease of T_N . In addition, the anomaly gets smeared out for low-impurity concentrations, especially in the case of Ir substitution, where it is completely suppressed at $x=0.03$. The effect of Rh substitution is less destructive: the anomaly is considerably spread out but still noticeable below 10 K for $x=0.05$. Incorporation of Re seems to have the least effect on the shape of the feature at T_N ;

FIG. 1. Normalized electrical resistivity $\rho(T)/\rho(300 \text{ K})$ vs temperature T data for $\text{URu}_{2-x}\text{Ir}_x\text{Si}_2$ compounds with various compositions x .

the transition is clearly seen for $x=0.05$, although it is broadened somewhat and is completely removed only for $x=0.1$. In contrast, the substitution of isoelectronic Os for Ru results in a completely different behavior: T_N increases with x , first slowly for $x \leq 0.04$ and then more rapidly for $x > 0.04$, reaching the value of 19.8 K for $x=0.1$, at which point the transition is enormously broadened. Assuming that the resistivity of URu_2Si_2 at 300 K does not substantially change upon substitution (at least up to $x=0.01$),²⁰ we can infer from the $\rho(300 \text{ K})/\rho(2 \text{ K})$ values listed in Table II that the increase of the residual resistivity ρ_0 at $T \gtrsim T_c$ depends strongly on the

FIG. 2. Normalized low-temperature electrical resistivity $\rho(T)/\rho(300 \text{ K})$ vs temperature T data for $\text{URu}_{2-x}\text{M}_x\text{Si}_2$ compounds with various compositions x . For clarity, data for some compositions are not shown.

FIG. 3. Temperature coefficient of electrical resistivity $(1/\rho)(d\rho/dT)$ of $\text{URu}_{2-x}\text{Rh}_x\text{Si}_2$ vs temperature T for selected compositions x . The SDW transition temperature T_N is defined as the temperature corresponding to the minimum in $(1/\rho)(d\rho/dT)$.

solute element and is the largest for Re. The incorporation of Rh and Ir atoms induces a moderate increase in ρ_0 , whereas Os atoms do not alter it significantly.

Shown in Figs. 4 and 5 are representative results of $\chi(T)$ measurements for $M=\text{Os}$ and Ir , respectively. The magnetic susceptibility exhibits single-ion Kondo behavior below 300 K, followed by a rounded maximum near 55 K that correlates with a similar maximum in the $\rho(T)$ data. However, the maximum in $\chi(T)$ occurs at a temperature 20 K lower than that in $\rho(T)$. The magnetic transition is characterized by a sudden but small decrease of $\chi(T)$ near $T_N \approx 17.5$ K, defined as the inflection point of the anomaly. The Curie-Weiss behavior above T_M is not influenced by alloying, and no clear trend is observed for Rh and Ir substitutions for the compositions investigated. In contrast, the magnetic susceptibility above 20 K increases in the $\text{URu}_{2-x}\text{Os}_x\text{Si}_2$ materials. The effect on T_N of transition-metal doping inferred from the $\chi(T)$ data is similar to that determined from the $\rho(T)$ data:

FIG. 4. Magnetic susceptibility χ vs temperature T for $\text{URu}_{2-x}\text{Os}_x\text{Si}_2$ compounds with various compositions x . Inset: χ vs T for $T \leq 25$ K.

broadening of the anomaly and a decrease (increase) of T_N for $M=\text{Rh}$, Ir , and Re (Os) as shown in the insets of Figs. 4 and 5. The substitution of Tc at $x=0.05$, as revealed by $\chi(T)$ data, depresses T_N to 16.2 K, a value close to that of $\text{URu}_{1.95}\text{Re}_{0.05}\text{Si}_2$. It is interesting to note that in the Os-doped samples, not only T_N , but also the magnitude of the susceptibility change associated with the transition, increases with x . With the exception of the $\text{URu}_{2-x}\text{Re}_x\text{Si}_2$ materials, the susceptibility reaches a plateau at lower temperatures and $\chi(0) \approx (2.5-3.0) \times 10^{-3} \text{ cm}^3/\text{mol}$ is of the same order as in URu_2Si_2 .

The magnetic behavior of the Re- and Tc-doped materials is anomalous. For $\text{URu}_{2-x}\text{Re}_x\text{Si}_2$ in the range $0 \leq x \leq 0.1$, the susceptibility at all temperatures increases and is accompanied by an upturn at low temperatures. With a further increase of x , the susceptibility at 300 K decreases; however, as the temperature is lowered

TABLE II. Characteristic temperatures T_M , determined from magnetic susceptibility χ and electrical resistivity ρ measurements, 0 K extrapolated values of the electronic specific heat coefficient γ , and residual resistivity ratios $\rho(300 \text{ K})/\rho(2 \text{ K})$ for selected samples in the $\text{URu}_{2-x}M_x\text{Si}_2$ alloy systems.

Compound	(K) (T_M) $_{\chi}$	(K) (T_M) $_{\rho}$	mJ/mol K ² γ	$\rho(300 \text{ K})/\rho(2 \text{ K})$
URu_2Si_2	55	79	65.5	24.6
$\text{URu}_{1.98}\text{Rh}_{0.02}\text{Si}_2$	60	79		9.1
$\text{URu}_{1.95}\text{Rh}_{0.05}\text{Si}_2$	51.8			9.6
$\text{URu}_{1.9}\text{Rh}_{0.1}\text{Si}_2$	49.4	69	105	8.2
$\text{URu}_{1.95}\text{Os}_{0.05}\text{Si}_2$	57.2	86		26.4
$\text{URu}_{1.9}\text{Os}_{0.1}\text{Si}_2$	66.4	92		17.9
$\text{URu}_{1.95}\text{Ir}_{0.05}\text{Si}_2$	55	79.5		13.5
$\text{URu}_{1.9}\text{Ir}_{0.1}\text{Si}_2$	60	90.5		9.1
$\text{URu}_{1.95}\text{Re}_{0.05}\text{Si}_2$	59.5	90		4.2
$\text{URu}_{1.9}\text{Re}_{0.1}\text{Si}_2$	59.1	89	70.5	4.9
$\text{URu}_{1.8}\text{Re}_{0.2}\text{Si}_2$	53.9	88.5		4.4
$\text{URu}_{1.95}\text{Tc}_{0.05}\text{Si}_2$	50

FIG. 5. Magnetic susceptibility χ vs temperature T for $\text{URu}_{2-x}\text{Ir}_x\text{Si}_2$ compounds with various compositions x . Inset: χ vs T for $T \leq 25$ K.

there is a crossover and the system again becomes more magnetic, displaying a large upturn in $\chi(T)$ below 10 K. A linear extrapolation to 0 K yields $\chi(0) \approx 6 \times 10^{-3} \text{ cm}^3/\text{mol}$, a value two times larger than that of URu_2Si_2 . The changes in $\chi(T)$ are greater in the $\text{URu}_{2-x}\text{Tc}_x\text{Si}_2$ series. For $x \leq 0.12$, the susceptibility decreases by $\sim 30\%$ at 300 K and shows a very weak temperature dependence. For $x = 0.05$, the rounded maximum shows significant broadening and is virtually nonexistent for $\text{URu}_{1.88}\text{Tc}_{0.12}\text{Si}_2$. This anomalous behavior of $\chi(T)$ appears to be the precursor of the ferromagnetic ordering we recently discovered in the $\text{URu}_{2-x}\text{Re}_x\text{Si}_2$ and $\text{URu}_{2-x}\text{Tc}_x\text{Si}_2$ systems in the composition range $0.4 \lesssim x \lesssim 1.4$.²¹

Inductive measurements of the superconducting transition temperature T_c for the $\text{URu}_{2-x}\text{M}_x\text{Si}_2$ materials yielded values slightly lower than those obtained from electrical resistivity measurements. In this work, T_c is

defined as the temperature where the magnitude of χ_{ac} has decreased by 50% of the total change associated with the superconducting transition. Normalized $\chi_{ac}/\chi_{ac}(0.1 \text{ K})$ versus T data are displayed in Fig. 6 for $M = \text{Rh}$. In general, the data reveal a progressive broadening of the superconducting transition as a function of impurity concentration x , especially in the Ir-substituted samples for $x > 0.03$ (data not shown). The substitution of transition metals $M = \text{Re}$, and Os for Ru , leads to a rapid depression of T_c , particularly in the case of Re , where T_c drops to 0.23 K for $x = 0.01$. In the case of Os substitutions, T_c decreases more gradually and is equal to 0.80 K for $x = 0.03$. The dependence of T_c on Rh and Ir composition x is similar, T_c first increases, passes through a maximum, and then decreases with further increase of x . However, T_c cannot be determined accurately beyond $x = 0.04$ in the $\text{URu}_{2-x}\text{Ir}_x\text{Si}_2$ series because of the broadening of the transition widths and the scatter in the $T_c(x)$ data. Doping with Rh at the level $x = 0.03$ results in a T_c that is considerably depressed, with a superconducting onset below 0.4 K. Also, a sample of $\text{URu}_{1.95}\text{Tc}_{0.05}\text{Si}_2$ was checked and found nonsuperconducting above 70 mK.

Specific heat C divided by T versus T^2 data below 20 K are shown in Fig. 7 for URu_2Si_2 , $\text{URu}_{1.9}\text{Re}_{0.1}\text{Si}_2$, and $\text{URu}_{1.9}\text{Rh}_{0.1}\text{Si}_2$. The substitution of 5 at. % Re or Rh for Ru in URu_2Si_2 hardly affects the specific heat above 18 K but suppresses the anomaly at T_N almost entirely. The jump at T_N is considerably reduced, broadened and transformed into a rounded maximum at ~ 12.6 K for $\text{URu}_{1.9}\text{Re}_{0.1}\text{Si}_2$ and an extremely broad shoulder below 10 K for $\text{URu}_{1.9}\text{Rh}_{0.1}\text{Si}_2$. The normal-state specific heat of URu_2Si_2 between 2 and 18 K can be described by

$$C = \gamma T + \beta T^3 + A \exp(-\Delta/T), \quad (1)$$

where γT , βT^3 , and $A \exp(-\Delta/T)$ represent, respectively, the electronic, lattice, and SDW-state contributions. Above T_N , the data can be fitted to $C = \gamma' T + \beta' T^3$ with $\gamma' = 112 \text{ mJ/mol K}^2$ and $\beta' = 0.382 \text{ mJ/mol K}^2$ ($\Theta_D = 294 \text{ K}$). A least-squares fit of the SDW contribution to the specific heat to

$$\delta C = A \exp(-\Delta/T) \quad (2)$$

in a manner described in Ref. 4 yields $A = 989 \text{ J/mol K} = 490\gamma T_N$ and $\Delta = 129 \text{ K} = 7.2T_N$. The jump in specific heat at 17.5 K is equal to $5.8 \text{ J/mol K} = 2.9\gamma T_N$, and the entropy $\Delta S = \int_0^{T_N} (\delta C/T) dT$ is estimated to be $980 \text{ mJ/mol K} = 0.170k_B \ln 2$ per formula unit. From the ratio of the ungapped γ above 18 K to the low temperature $\gamma = 65.5 \text{ mJ/mol K}^2$ obtained by extrapolating the normal-state data above 1.5 K to $T = 0$, it has been estimated that 40% of the Fermi surface is removed at T_N by the transition to the SDW state.

The jump in the specific heat at $T_N \approx 13 \text{ K}$ in $\text{URu}_{1.9}\text{Re}_{0.1}\text{Si}_2$ is equal to $1.3 \text{ J/mol K} = 1.1\gamma T_N$, a value much smaller than in pure URu_2Si_2 . The data above 13 K can be described by $C = \gamma' T + \beta' T^3 + \alpha' T^5$ with $\gamma' = 90 \text{ mJ/mol K}^2$, $\beta' = 0.345 \text{ mJ/mol K}^4$ ($\Theta_D = 304 \text{ K}$), and $\alpha' = 4.91 \times 10^{-4} \text{ mJ/mol K}^6$. Following the same method

FIG. 6. Magnetic susceptibility χ_{ac} vs temperature T for $\text{URu}_{2-x}\text{Rh}_x\text{Si}_2$ compounds with various compositions $x \leq 0.02$ in zero applied magnetic field.

FIG. 7. Specific heat C divided by temperature T vs T^2 for URu_2Si_2 and $\text{URu}_{1.9}\text{M}_{0.1}\text{Si}_2$ with $M=\text{Rh}$ and Re . Inset: C/T vs T^2 for $T \leq 4$ K.

used for URu_2Si_2 , a least-squares fit of the SDW part of the specific heat to Eq. (2) yields $A=6.1$ J/mol K and $\Delta=17$ K. In this case, the instability removes only $\sim 25\%$ of the Fermi surface and the entropy associated with the transition is estimated to be 290 mJ/mol K $= 0.05k_B \ln 2$. The specific heat of $\text{URu}_{1.9}\text{Rh}_{0.1}\text{Si}_2$ is well described between 14 and 22 K by $C=\gamma'T+\beta'T^3$ with $\gamma'=130$ mJ/mol K² and $\beta'=0.403$ mJ/mol K⁴ ($\Theta_D=289$ K). The gap contribution δC can still be fitted to Eq. (2) with $A=1.2$ J/mol K and $\Delta=4$ K. Less than 20% of the Fermi surface is removed in this case, and the transition, although very broad, still involves an entropy of about 270 mJ/mol K, close to that of $\text{URu}_{1.9}\text{Re}_{0.1}\text{Si}_2$. The low-temperature data displayed in the inset of Fig. 7 reveal an upturn below 1 K in the Re-doped material that correlates with a similar upturn in the magnetic susceptibility. A linear extrapolation of the C/T versus T^2 from above 1 to 0 K yields an electronic-specific-heat coefficient $\gamma=71$ mJ/mol K² for $\text{URu}_{1.9}\text{Re}_{0.1}\text{Si}_2$ and 105 mJ/mol K² for $\text{URu}_{1.9}\text{Rh}_{0.1}\text{Si}_2$.

DISCUSSION

The magnetic transition at T_N , associated with the development of a SDW state is strongly affected by transition-metal M substitution at the Ru sites. The transition is smeared out by very small impurity concentrations. A plot summarizing $T_c(x)$ and $T_N(x)$ for all of the transition-metal substitutions investigated is shown in Fig. 8. On the basis of chemical pressure arguments alone, one would expect that the effect of substitution on T_c or T_N would be similar for all solutes since they all have metallic radii larger than that of Ru ($r_{\text{Ru}}=1.339$ Å, $r_{\text{Rh}}=1.345$ Å, $r_{\text{Re}}=1.375$ Å, $r_{\text{Tc}}=1.360$ Å, $r_{\text{Os}}=1.353$ Å, and $r_{\text{Ir}}=1.357$ Å).²² However, the fact that T_N increases with x for $M=\text{Os}$ and decreases with x for $M=\text{Rh}$, Re , Tc , and Ir in the range $0 \leq x \leq 0.1$ indicates that chemical pressure is not the prime factor influencing T_N .

The large spacing between U atoms in heavy-electron

FIG. 8. Impurity concentration x dependence of T_N and T_c for $\text{URu}_{2-x}\text{M}_x\text{Si}_2$ ($M=\text{Rh}$, Os , Re , and Ir). Closed circles represent $T_c(x)$ data from ac magnetic-susceptibility measurements. Open circles, triangles, and inverted triangles represent $T_N(x)$ data from electrical resistivity, magnetic susceptibility, and specific-heat measurements, respectively. The solid lines are guides to the eye.

compounds rules out a direct overlap of the f -electron wave functions so that f -level broadening can only occur through hybridization with conduction-electron states. The variation of the number of conduction electrons modifies the degree of hybridization and, in turn, the width of the f level given by $\Gamma=\pi\langle V^2\rangle N(0)$, where V is the hybridization matrix element and $N(0)$ the density of states at the Fermi level (for one spin orientation). Examination of the data reveals that the SDW state in URu_2Si_2 is very sensitive to U 5*f* ligand hybridization. The increase of the number of conduction electrons via incorporation of Rh and Ir leads to a depression of T_N and a deterioration of the SDW state for $0 \leq x \leq 0.1$, as revealed by the smearing of the anomaly at T_N . The decrease of conduction-electron density through substitution of Re or Tc also leads to a depression of T_N accompanied this time by an upturn in the susceptibility below

10 K. However, the incorporation of isoelectronic Os atoms, which leaves the conduction-electron density and in turn the degree of hybridization unchanged, is found to increase T_N as well as the amplitude of the transition. The increase of the latter may be due to an increase in the SDW energy gap below T_N .

The inverse correlation between T_c and T_N displayed by the Ir- and Rh-substituted systems for $0 \leq x < 0.01$ and most notably by $\text{URu}_{2-x}\text{Os}_x\text{Si}_2$ for $0 \leq x < 0.1$ is consistent with the picture of two ordered electronic states competing for portions of the Fermi surface. In the $\text{URu}_{2-x}\text{Re}_x\text{Si}_2$ system, both T_c and T_N decrease. It is noteworthy that the fraction of the Fermi surface removed by the transition and the energy gap Δ both decrease with x at a faster rate than T_N . Assuming that a decrease in T_N is associated with a decrease in the fraction of electron states involved in the formation of a SDW rather than a decrease in the coupling constant, then the increase of the electronic specific-heat coefficient γ in the Re- and Rh-doped compounds can be accounted for by a larger density of states available below T_N as a consequence of a gap opening over a smaller fraction of the Fermi surface. A mean-field treatment of the competition between superconductivity and CDW formation involving partial gapping of the Fermi surface was developed by Bilbro and McMillan²³ and applied to the pressure dependence of T_c and the structural transition temperature of the *A*-15 compounds²³ and Chevrel phases of the type $\text{Eu}_{1-x}\text{Sn}_x\text{Mo}_6\text{S}_8$.²⁴ The same treatment was extended by Machida²⁵ to the SDW case. The proposed relation between T_c and T_N can be written as $T_c^n T_N^{1-n} = T_{c0}$, where T_{c0} is the superconducting transition temperature in the absence of a gap and n is the ungapped fraction of the Fermi surface.

The very small entropy ($\sim 0.01 R \ln 2$ per mole U) associated with the magnetic transition in the $\text{URu}_{2-x}\text{M}_x\text{Si}_2$ compounds cannot be accounted for by localized spin models, for which the entropy removed by the transition is expected to be $R \ln(2S+1)$. Overhauser pointed out²⁶ that the phase transition from a paramagnetic state to a spin-density wave within the context of a nesting model would have an entropy much smaller than $R \ln(2S+1)$. In addition, the negligible effect of a magnetic field on the 17.5-K transition in a polycrystalline sample of URu_2Si_2 reported by Maple *et al.*⁴ is similar to the result found in Cr, where the SDW transition temperature is independent of magnetic field to values as high as 16 T.²⁷ However, the same experiment carried out on a single crystal of URu_2Si_2 revealed a 2% decrease of T_N when a field of 6 T was applied along the *c* axis.²⁸ In a recent review article, Fawcett²⁹ pointed out that the spin paramagnetism for a nesting model is the only term in $\chi(T)$ affected by the formation of a SDW and is smaller than the orbital paramagnetism. This is consistent with the small drop in $\chi(T)$ at T_N for the $\text{URu}_{2-x}\text{M}_x\text{Si}_2$ alloy systems. The increase of the electrical resistivity with decreasing temperature around T_N was first recognized in Cr by Trego and Mackintosh³⁰ as being due to the formation of an energy gap on the nesting part of the Fermi surface, which decreases the effective number of carriers.

It was suggested that the resistivity of URu_2Si_2 could be fit by a T^2 term associated with the low-temperature Fermi-liquid character and an exponential contribution preceeded by a temperature-dependent factor appropriate for an antiferromagnet with energy gap Δ .³ The size of the gap in URu_2Si_2 , estimated from far-infrared reflectance measurements,³¹ is between 5.6 and 7.5 meV, which is comparable to the value of 11 meV inferred from specific-heat measurements, and the shape of its energy dependence is similar to that of the energy gap observed in the SDW state of Cr. However, moment-polarized electron-energy band-structure calculations by Norman *et al.*³² predict that gapping occurs only when the ordered magnetic moment exceeds $1\mu_B$ and, moreover, do not indicate any Fermi-surface nesting.

The thermodynamics of a SDW state closely resembles that of a CDW state. In particular, there is a gap in the single-particle excitation that is described by the BCS equation and a collective mode formed by electron-hole pairs. A Ginzburg-Landau-type microscopic model has been developed by McMillan³³ to describe the charge-density wave in $2H\text{-TaSe}_2$. For a triple-CDW state, the heat-capacity jump is given by

$$\delta C = 14.1 N(0) k_B^2 T_N, \quad (3)$$

and the change in susceptibility due to the opening of the gap is

$$\delta \chi = 2.6 N(0) \mu_B^2. \quad (4)$$

In order to compare the model with experiment in URu_2Si_2 , we first find $N(0) \approx 32$ states/eV-U atom from Eq. (3) and the experimental value $\delta C = 5.8$ J/mol K for URu_2Si_2 . Using Eq. (4), the model then yields $\delta \chi \approx 2.7 \times 10^{-3}$ cm³/mol, which is approximately four times larger than the experimental value of 0.7×10^{-3} cm³/mol. The model also predicts an energy gap at zero temperature $\Delta \approx 1.75 k_B T_N = 2.6$ meV, a factor of 2 smaller than the value estimated from far-infrared reflectance measurements and a factor of 4 smaller than the value estimated from the specific-heat data.

In summary, the effects of various transition-metal substitutions in URu_2Si_2 have been investigated. The hybridization between *5f* and conduction-electron states is found to have a strong effect on the SDW state, of which the characteristic temperature T_N decreases with either increase or decrease of the degree of hybridization. In contrast, isoelectronic Os substitutional atoms induce an increase in T_N . The particularly large inverse correlation between T_N and T_c in the Os-doped materials is consistent with two transitions competing for electronic states over the Fermi surface. The increase of γ , the electronic coefficient of the specific heat, below T_N in $x = 0.1$ Re- and Rh-doped materials is consistent with the SDW state forming over a smaller fraction of the Fermi surface.

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