Magnetism and spin fluctuation effects in heavy-fermion $CeRu_2Si_2$ induced by partial substitution of Ru and Si

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The effect of chemical substitution in $CeRu_2Si_2$, a well-studied heavy-fermion system, has been investigated through magnetic susceptibility and x-ray diffraction measurements in the systems $CeRu_xSi_2$, $CeRu_{2-x}Os_xSi_2$, $CeRu_2Si_{2-x}C_x$, and $CeRu_2Si_{2-x}Ge_x$. Replacing silicon by carbon and germanium generates the normal chemical-pressure effect, namely Ce atoms in $CeRu_2Si_{2-x}C_x$ and $CeRu_2Si_{2-x}Ge_x$ are, respectively, less and more magnetic than in $CeRu_2Si_2$. With increasing Ge concentration, $CeRu_2Si_{2-x}Ge_x$ first exhibits a larger low-temperature susceptibility than that in pure $CeRu_2Si_2$, then goes into an antiferromagnetic phase, and finally becomes ferromagnetic. Electronic effects are more important than the chemical-pressure effect in $CeRu_{2-x}Os_xSi_2$ since the lattice constants of $CeOs_2Si_2$ are very nearly the same as those of $CeRu_2Si_2$. It is conjectured that $CeRu_2Si_{2-x}Ge_x$ may be the first Ce-based heavy-fermion system having a magnetic ground state.

INTRODUCTION

Rare-earth-metal ternary silicides with the $ThCr_2Si_2$ tetragonal structure exhibit a rich variety of physical phenomena such as Kondo-lattice behavior, mixed valence, and heavy-fermion superconductivity. $CeRu_2Si_2$ is one such material. We had reported earlier the Kondo-lattice behavior[1] of this system as observed in our susceptibility and resistivity measurements. The magnitude of the low-temperature electronic specific-heat coefficient $\gamma = 385$ mJ/(mole Ce) K^2 established[2] clearly the heavy-fermion nature of this system. However, in contrast with isostructural heavy-fermion superconductor $CeCu_2Si_2$, this system does not superconduct down to 20 mK and remains normal.[1,3] The system has also been compared, in many respects, to UPt_3,[4] another heavy-fermion superconductor. Alloying $CeRu_2Si_2$ with La and Y has been tried and studied;[5] the resulting modifications in the behavior of $CeRu_2Si_2$, can be understood in terms of normal chemical-pressure effects in mixed-valence materials, viz., substitution by smaller (larger) ions pushes the system to a higher (lower) valence as was first shown[6] in the case of $Sm_{1-x}R_x^{3+}S$ (R denotes a rare-earth ion). We have investigated a number of substituted systems, namely, $CeRu_{2-x}Os_xSi_2$, $CeRu_2Si_{2-x}C_x$, and $CeRu_2Si_{2-x}Ge_x$. Nonstoichiometric $CeRu_xSi_2$ has also been investigated. The aim of this paper is to report the results of these investigations and emphasize the effect of various dopant atoms on the physical properties of the parent heavy-fermion system $CeRu_2Si_2$.

EXPERIMENTAL

Samples were prepared by melting the required amounts of various constituents, viz., Ce (99.9% pure), C (99.999% pure), Si (99.999% pure), Ge (99.999% pure), Ru (99.99% pure), and Os (99.99% pure) in an arc furnace under an argon atmosphere. The buttons were flipped and remelted six times to achieve good homogeneity. Weight losses during melting were less than 1%. The nominal compositions of the various alloys studied in this work are $CeRu_xSi_2$ ($x = 1.9, 2.0, 2.1$), $CeRu_2Si_{2-x}Ge_x$ ($x = 0.1, 0.2, 0.5, 1.0, 1.5, 2.0$), $CeRu_2Si_{2-x}C_x$ ($x = 0.1$), and $CeRu_{2-x}Os_xSi_2$ ($x = 0.05, 0.1, 0.3, 0.5, 2.0$). $CeRu_xSi_2$ samples and Os-containing samples were annealed at ~ 1100 K for 8 days. X-ray measurements were carried out at room temperature with a Siemens automatic diffraction spectrometer. Magnetization and magnetic susceptibility measurements were performed in the range 5—300 K using a Faraday microbalance. The instrument was calibrated using a National Bureau of Standards χ standard (platinum) and an appropriate bucket correction was applied while calculating the susceptibility.

RESULTS

X-ray diffraction patterns of all the samples investigated confirmed the single-phase nature of all the compositions studied. The lattice parameters a and c obtained by least-squares fitting of high-angle lines ($2\theta > 30°$), and the c/a ratio are shown in Table I. Figure 1 shows the variation of a, c, c/a, and the unit-cell volume as a function of x in the alloy $CeRu_{2-x}Os_xSi_2$ and $CeRu_2Si_{2-x}Ge_x$. Both of these alloy systems exhibit deviations from Vegard's law. Hiebl *et al.* had also earlier reported[7] this feature in $CeRu_{2-x}Os_xSi_2$. In general, Vegard's law is not obeyed, which is characteristic of mixed-valence systems.

It is clear from Fig. 1 that substitution of Si and Ru by the bigger ions Ge and Os, respectively, does not have the same effect. In the germanium-doped samples, both a and c increase with germanium concentration. The osmium doping decreases a but increases c. As a consequence of this, the lattice-cell volume of the system $CeRu_{2-x}Os_xSi_2$ does not vary much with x. See Table I also.

Figures 2 and 3 display the temperature dependence of the magnetic susceptibility of $CeRu_xSi_2$ and $CeRu_2Si_{2-x}Y_x$ (Y = C,Ge), respectively. The high-

TABLE I. Crystallographic and magnetic data for substituted $CeRu_2Si_2$. T_{SF} and T_{SF}^* are spin-fluctuation temperatures as defined in the text and T_C and T_N are magnetic ordering temperatures.

Compound	a (Å)	c (Å)	c/a	Vol. (Å^3)	T_{SF} (K)	T_{SF}^* (K)	T_C, T_N (K)
$CeRu_{1.9}Si_2$	4.193	9.793	2.336	172.17	25	28	
$CeRu_2Si_2$	4.195	9.796	2.335	172.39	18	23	
$CeRu_{2.1}Si_2$	4.193	9.794	2.336	172.19	15	14	
$CeRu_2Si_{1.9}C_{0.1}$	4.190	9.791	2.337	171.84	20	30	
$CeRu_2Si_{1.9}Ge_{0.1}$	4.197	9.807	2.337	172.75		8	
$CeRu_2Si_{1.8}Ge_{0.2}$	4.202	9.808	2.334	173.18			
$CeRu_2Si_{1.5}Ge_{0.5}$	4.207	9.846	2.340	174.26			$T_N=8.0$
$CeRu_2SiGe$	4.224	9.899	2.344	176.62			$T_M=9.2$[a]
$CeRu_2Si_{0.5}Ge_{1.5}$	4.245	9.968	2.348	179.62			$T_C=10.0$
$CeRu_2Ge_2$	4.269	10.035	2.351	182.88			$T_C=11.0$
	4.263[b]	10.08[b]					
$CeRu_{1.95}Os_{0.05}Si_2$	4.194	9.796	2.336	172.30	28	57	
$CeRu_{1.9}Os_{0.1}Si_2$	4.192	9.791	2.336	172.05	45	85	
$CeRu_{1.7}Os_{0.3}Si_2$	4.191	9.795	2.337	172.04	67	100	
$CeRu_{1.5}Os_{0.5}Si_2$	4.189	9.796	2.339	171.89	115		
	4.190[c]	9.800[c]					
$CeOs_2Si_2$	4.160	9.838	2.364	170.25			
	4.160[c]	9.843[c]					

[a]See the text.
[b]Reference 8.
[c]Reference 7.

temperature (300 K) susceptibility is nearly the same for all other compositions. An excess of ruthenium in $CeRu_2Si_2$ increases the susceptibility at all temperatures, whereas a deficiency of ruthenium generates exactly the opposite effect (Fig. 2); carbon substitution, as shown in Fig. 3, decreases the susceptibility which is consistent with what one should expect. Germanium-doped material $CeRu_2Si_{2-x}Ge_x$ exhibits a variety of magnetic behavior; initially with small x (~ 0.1) the Ce moment becomes more stable. With a further increase in x, the system undergoes a magnetic transition, the nature of which depends upon the value of x. For example $CeRu_2Si_{1.5}Ge_{0.5}$ shows antiferromagnetic ordering below $T_N=8$ K and $CeRu_2Si_{0.5}Ge_{1.5}$ becomes ferromagnetically ordered below $T_c=10$ K. The type of magnetic ordering is inferred not only from the nature of the $\chi(T)$ versus T plot but also from the magnetization of the sample measured as a function of the applied field H ($0 \leq H \leq 8$ kG) shown in Fig. 4. The material $CeRu_2SiGe$ exhibits a rather complex behavior in that $\chi(T)$ of this system shows a peak at 9 K, just as in an antiferromagnet, and increases again at still

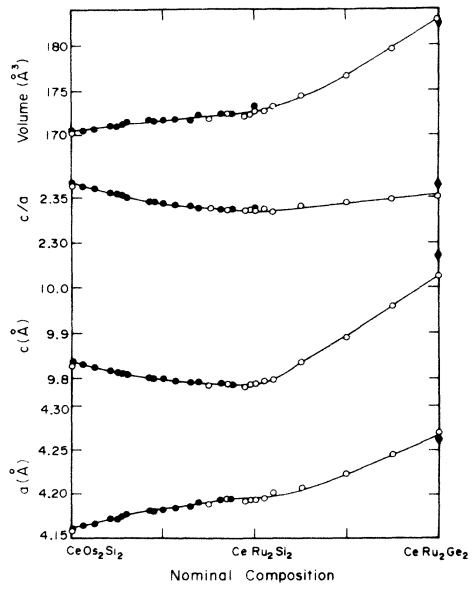

FIG. 1. Variation of the lattice parameters a and c, the a/c ratio and unit-cell volume for $CeRu_{2-x}Os_xSi_2$ and $CeRu_2Si_{2-x}Ge_x$ (○ this work, ● Ref. 7, ♦ Ref. 8).

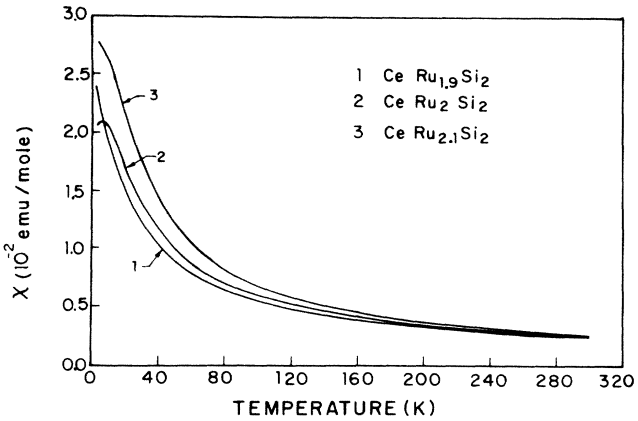

FIG. 2. Susceptibility versus temperature for $CeRu_xSi_2$.

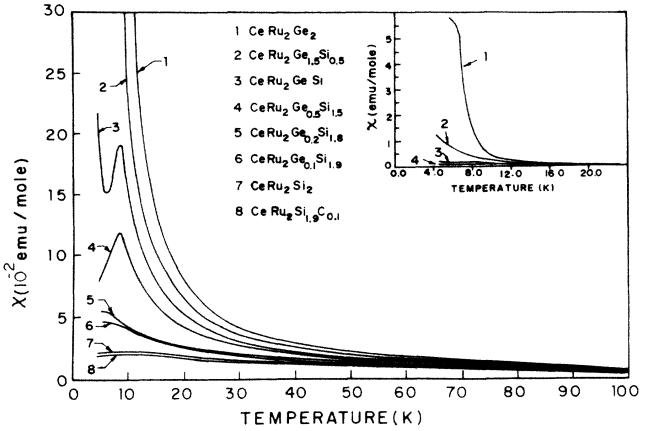

FIG. 3. Susceptibility versus temperature for C- and Ge-substituted $CeRu_2Si_2$. Inset shows low-temperature data for magnetic Ge-substituted samples.

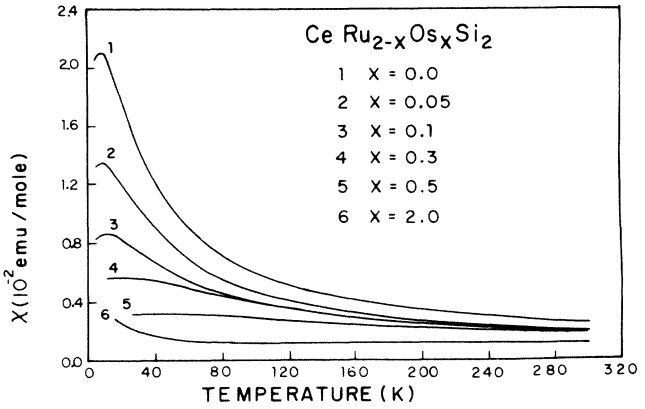

FIG. 5. Susceptibility versus temperature for $CeRu_{2-x}Os_xSi_2$.

lower temperatures. The magnetization behavior also is not simple. It is not clear whether the peak at 9 K corresponds to spin-glass freezing which at lower temperature gives way to yet another type of magnetic ordering. Further experiments are underway to clarify the magnetic behavior of this composition.

The magnetic susceptibility, as a function of temperature, measured on the osmium-substituted samples $CeRu_{2-x}Os_xSi_2$ is displayed in Fig. 5. It is clear from the figure that with increasing x, the susceptibility decreases. Though the metallic radii of Ru and Os are very similar ($r_{Ru}\simeq 1.34$ Å and $r_{Os}\simeq 1.35$ Å), the magnetic properties of the two systems $CeOs_2Si_2$ and $CeRu_2Si_2$ are very different. On the basis of chemical pressure effects alone, just as in Ge-doped samples, one would have expected that introduction of osmium in the lattice would enhance the susceptibility. The maximum in the susceptibility, which occurs at ~ 8 K in pure $CeRu_2Si_2$, is also pushed towards high temperature. For instance $T(\chi_{max})=14$ K for $x=0.1$ and $T(\chi_{max})=25$ K for $x=0.3$. The susceptibility of the full osmium sample does not show a clear maximum, which is in agreement with the results of Hieble *et al.*[7]

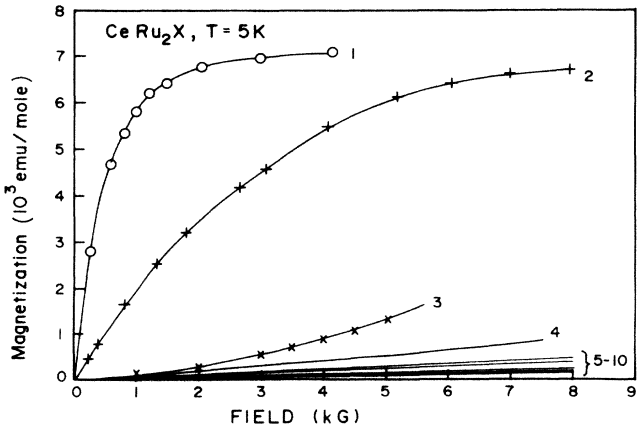

FIG. 4. Magnetization versus field for C- and Ge-substituted $CeRu_2Si_{2-x}X_x$ [$X_x=Ge_2(1)$, $Ge_{1.5}(2)$, $Ge(3)$, $Ge_{0.5}(4)$, $Ge_{0.2}(5)$, $Ge_{0.1}(6)$, and $C_{0.1}(10)$] and $CeRu_xSi_2$ [$x=2.1(7)$, 2(8), and 1.9(9)].

DISCUSSION

In Kondo-lattice systems, the magnetic susceptibility is described in terms of T_{SF}, the spin-fluctuation temperature, which is defined as[9]

$$T_{SF}=\frac{C}{2\chi(0)}$$

where C is the Curie constant for free ions (in this case Ce^{3+} ions) and $\chi(0)$ is $\chi(T)$ of the system at $T=0$ K. Alternatively the spin-fluctuation temperature T^*_{SF} is also defined[10] as the temperature such that

$$\frac{T\chi(T)}{C}=\frac{1}{2}\ .$$

Table I shows the values of T_{SF} and T^*_{SF} obtained using both of these procedures in each case studied here. We had reported earlier a lower value (~ 5 K) of T_{SF} for $CeRu_2Si_2$, which, according to the present analysis, turns out to be somewhat higher, i.e., T_{SF} or $T^*_{SF}\simeq 20$ K. From the measured susceptibility of $CeRu_{2.1}Si_2$ and $CeRu_{1.9}Si_2$, it follows that an excess (deficiency) of ruthenium decreases (increases) T_{SF} of Ce in $CeRu_2Si_2$. It is instructive to compare this behavior with that of $CeCu_2Si_2$. Vacancies at the copper sites have been shown to depress T_{SF} and, therefore, to be responsible for the suppression of superconductivity in the heavy-fermion system $CeCu_2Si_2$.[11]

It has been suggested that low-temperature physical properties of nearly trivalent cerium systems (which do not undergo a magnetic ordering at low temperatures) are similar to those of a Fermi liquid.[10] The magnetic susceptibility of such materials obeys a scaling behavior that can be expressed as $T\chi(T)/C=f(T/T^*_{SF})$, where f is a universal function. This means that the quantity $T\chi(T)/C$, measured for such materials and plotted as a function of T/T^*_{SF}, follows a unique curve. This scaling law is valid when the change in valence, as a function of

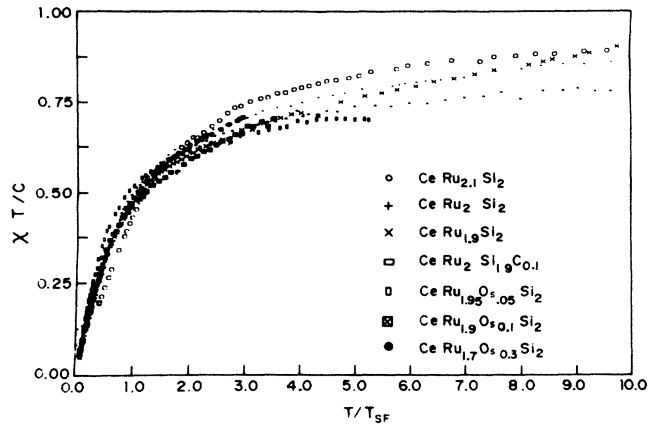

FIG. 6. $\chi T/C$ vs T/T^*_{SF} for mixed-valence pseudoternary $CeRu_2Si_2$ (see the text).

temperature, is not too big and the system stays nonmagnetic at low temperature. Such a behavior has been observed earlier[10] for the system $CeSn_{3-x}In_x$ with values of x that do not induce a magnetic ordering and give rise to an enhanced Pauli susceptibility at low temperatures.

Figure 6 shows the plots of $T\chi(T)/C$ versus T/T^*_{SF} for many materials studied here. The scaling behavior is roughly valid. The scatter that one sees at high temperatures in some cases is because of two reasons: Firstly, we have not subtracted the non-$4f$ contribution to the susceptibility. Secondly, if T_{SF} is high, one needs $\chi(T)$ at very high temperatures to obtain a reliable and accurate value of T^*_{SF}. We also would like to point out that usually in such studies one plots $T\chi(T)/C$ versus $\ln(T/T^*_{SF})$ rather than plotting $T\chi(T)/C$ versus T/T^*_{SF}. This procedure has a smoothing effect due to which the data apparently seem to follow the universal behavior rather closely. Values of T^*_{SF} for various compositions obtained in our work are given in Table I.

It is instructive to examine the first-nearest-neighbor environment of Ce in $CeRu_2Si_2$ and $CeOs_2Si_2$. There are eight transition-metal (TM) (Ru,Os) neighbors at a distance of $[(a/2)^2+(c/4)^2]^{1/2}$ Å and eight Si neighbors at a distance of $[a^2/2+c^2(\frac{1}{2}-z)^2]^{1/2}$ Å. The variable parameter z has to be determined experimentally, either by a single-crystal x-ray structural investigation or by extended x-ray-absorption fine-structure and is therefore not available generally. For these two materials, however, values of z have been determined by single-crystal work; $z=0.365$ for $CeRu_2Si_2$ (Ref. 12) and $z=0.371$ for $CeOs_2Si_2$ (Ref. 13). Using these values of z, one can calculate the Ce-Si and Ce-TM distances in these two materials. They are as follows: Ce-Si=3.248 Å, Ce-Ru=3.224 Å in $CeRu_2Si_2$ and Ce-Si=3.204 Å, Ce-Os=3.22 Å in $CeOs_2Si_2$.

Considering the atomic radii of Ru and Os ($r_{Ru}=1.34$ Å and $r_{Os}=1.35$ Å), one would expect that the interatomic distances in $CeOs_2Si_2$ should be slightly larger than those in $CeRu_2Si_2$. This, however, is not the case as discussed above. Thus, it is clear that in $CeOs_2Si_2$ it is not the chemical pressure effect which is responsible for the nearly "tetravalent" state of Ce. The Ce-Si distance in $CeOs_2Si_2$ is 1.5% shorter than that in $CeRu_2Si_2$ so the Ce-Si overlap is increased. The Ce-Os distance is exactly the same as the Ce-Ru distance, so the Ce-Os overlap is also increased (because $r_{Os}>r_{Ru}$). There are increased overlaps between Ce-Si and Ce-TM in $CeOs_2Si_2$ as compared to that in $CeRu_2Si_2$ which drives cerium towards tetravalence. In this structure the TM-Si overlap is always strong (the TM-Si distance is smaller than $r_{TM}+r_{Si}$—i.e., Os-Si=2.40 Å <1.35 Å $+1.32$ Å and Ru-Si=2.38 Å <1.34 Å $+1.32$ Å). Moreover, the Si-Si distance 2.651 Å in $CeRu_2Si_2$ (and 2.535 Å in $CeOs_2Si_2$) is larger, (respectively, smaller) than $2r_{Si}$. It seems that small changes in the overlap greatly modify the possibilities of electronic exchange in $CeOs_2Si_2$ as compared to $CeRu_2Si_2$.

It should be noted that in both of these materials, the Ce-Ce distance is much larger than the Hill limit,[14] and therefore the direct overlap of $4f$ wave functions located on different Ce atoms is not responsible for the delocalization of the $4f$ electron or, to express it equivalently, for the formation of a narrow $4f$ band. The delocalization essentially occurs through hybridization of the f-electron wave function with the sp or s wave functions of the neighboring (in this case Si) atoms.

The enhancement of the paramagnetic susceptibility of germanium-doped samples $CeRu_2Si_{2-x}Ge_x$ over that of $CeRu_2Si_2$ suggests that small concentrations of germanium enhance the heavy-fermion character of $CeRu_2Si_2$. This follows from the fact that $\chi(0)$ and γ of the heavy-fermion systems are related to each other in more or less a systematic fashion. Thus, enhancement of $\chi(0)$ strongly suggests enhancement of γ also. Further, one may suspect that with gradual introduction of germanium, it may be possible to induce a magnetic order in the system while still retaining its heavy-fermion character. This is important since none of the Ce-based heavy-fermion system known so far has a magnetic ground state. On the other hand, uranium-based heavy-fermion systems [such as U_2Zn_{17} (Ref. 15)] having a magnetic ground state are known. We have, therefore, undertaken a detailed investigation of the physical properties of the $CeRu_2Si_{2-x}Ge_x$ system varying Ge concentration more systematically and gradually. Further studies on L_{III}-edge measurements and possible occurrence of superconductivity in samples with low osmium concentration are underway and will be reported elsewhere.

To summarize, the effect of various substitutions in $CeRu_2Si_2$ have been investigated. It is concluded that the nearly tetravalent character of Ce in $CeOs_2Si_2$ vis-à-vis the nearly trivalent character of Ce in $CeRu_2Si_2$, is due to the increased overlap of Ce $4f$ wave function with silicon and metal wave functions. $CeRu_2Si_{2-x}Ge_x$ exhibits most interesting behavior in that with small concentrations of Ge magnetic susceptibility increases without the system becoming magnetically ordered. This indicates that γ also should become enhanced. Possibility and implications of $CeRu_2Si_{2-x}Ge_x$ (with a certain value of x) being a heavy-fermion system with a magnetic ground state have been pointed out.

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