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Spin fluctuation effects in substituted $CeRu_2Si_2$ and $YbPd_2Si_2$ alloys

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Abstract. Effects of chemical substitution in $CeRu_2Si_2$, a well-studied heavy fermion system and $YbPd_2Si_2$ have been investigated through magnetic susceptibility and x-ray diffraction in the systems $CeRu_xSi_2$, $CeRu_{2-x}Os_xSi_2$, $CeRu_2Si_{2-x}Ge_x$ and $YbPd_2Si_{2-x}Ge_x$. Replacing silicon by germanium generates normal chemical pressure effect, namely, Ce and Yb atoms in $CeRu_2Si_2$ and $YbPd_2Si_2$ became more and less magnetic respectively. With increasing Ge concentration, $CeRu_2Si_{2-x}Ge_x$ exhibits larger susceptibility at low temperature, goes to an antiferromagnetic state and finally becomes ferromagnetic. In $YbPd_2Si_{2-x}Ge_x$, increasing Ge concentration drives Yb atoms to more divalent state. Electronic effects are more pronounced in $CeRu_{2-x}Os_xSi_2$ though $CeRu_2Si_2$ and $CeOs_2Si_2$ have very nearly the same lattice parameters. It is conjectured that $CeRu_2Si_{2-x}Ge_x$ may be the first Ce-based heavy fermion having a magnetic ground state.

Keywords. Spin fluctuation; chemical pressure effect; mixed valence; magnetic susceptibility.

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1. Introduction

Rare earth ternary silicides with $ThCr_2Si_2$ tetragonal structure, exhibit a rich variety of physical phenomena such as Kondo lattice behaviour, mixed valence and heavy fermion superconductivity. $CeRu_2Si_2$ is one such material. We had reported earlier the Kondo lattice behaviour (Gupta *et al* 1983) of this system through our susceptibility and resistivity measurements. The magnitude of low temperature electronic specific heat coefficient $\gamma = 385$ mJ/mol Ce-K^2 established (Thompson *et al* 1985) 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 (Gupta *et al* 1983; Tholence *et al* 1985). The system has also been compared, in many respects, to UPt_3 (Flouquet *et al* 1985), another heavy fermion superconductor. $YbPd_2Si_2$ has been reported to show effects of valence fluctuation with a peak in susceptibility around 30 K (Sampathkumaran *et al* 1984). It is interesting to point out that superconductivity has been reported in $YbPd_2Ge_2$. There are, however, some doubts about the single phase nature of the sample (Hull *et al* 1981). Alloying $CeRu_2Si_2$ with La and Y has been tried and studied (Besnus *et al* 1985). The resulting modifications in the behaviour of $CeRu_2Si_2$ can be understood in terms of

The authors felicitate Prof. D S Kothari on his eightieth birthday and dedicate this paper to him on this occasion.

normal chemical pressure effects in mixed valent materials, viz substitution by smaller (larger) ion pushes the system to higher (lower) valence as it was first shown (Jayaraman 1974) in the case of $Sm_{1-x}RE_x^{3+}S$ (RE = rare earth). We have investigated a number of substituted systems, namely, $CeRu_{2-x}Os_xSi_2$, $CeRu_2Si_{2-x}C_x$, $CeRu_2Si_{2-x}Ge_x$ and $YbPd_2Si_{2-x}Ge_x$. Nonstoichiometric $CeRu_xSi_2$ also has 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 systems, $CeRu_2Si_2$ and spin fluctuation system $YbPd_2Si_2$.

2. Experimental

Samples were prepared by melting the required amounts of various constituents, viz Ce (99·9 %), Yb (99·9 %), C (99·999 %), Si (99·999 %), Ge (99·999 %), Ru (99·99 %) and Os (99·99 %) in an arc furnace under argon atmosphere. The buttons were flipped and remelted six times to achieve good homogeneity. Weight losses during melting were less than 1 % except in the Yb containing samples where excess Yb had to be added to compensate losses during melting. 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), $YbPd_2Si_{2-x}Ge_x$ (x = 0·05, 0·1, 0·3), $CeRu_2Si_{2-x}C_x$ (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 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 an NBS χ-standard (platinum) and an appropriate bucket correction was applied while calculating the susceptibility.

3. Results

X-ray diffraction patterns of 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 c/a ratio are shown in table 1. 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 these alloy systems exhibit deviation from Vegard law. Hiebl *et al* (1984) had also earlier reported this feature in $CeRu_{2-x}Os_xSi_2$. In general, Vegard law is not obeyed which is characteristic of mixed valent system.

It is clear from figure 1 that substitution of Si and Ru by bigger ions Ge and Os, respectively, does not have the same effect. In the germanium-doped samples, both a and c increase with germanium concentrations. The osmium doping decreases a but increases c. As a consequence, the lattice cell volume of the system $CeRu_{2-x}Os_xSi_2$ does not vary much with x (see table 1 also). The x-ray patterns of $YbPd_2Si_{2-x}Ge_x$ show some line broadening, thereby indicating difficulty in forming single phase $YbPd_2Ge_2$ sample.

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 temperature ($\sim$ 300 K) susceptibility is nearly same for all other compositions. Excess of ruthenium

Table 1. Crystallographic and magnetic data for substituted alloys. 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 (A)	c (A)	c/a	Vol. (A^3)	T_{sf} (K)	T^*_{sf} (K)	T_M (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	—	—	$T_M = 9·2$
$CeRu_2Si_{0.5}Ge_{1.5}$	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††	10·08††					
$CeRu_{1.95}Os_{0.05}Si_2$	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†	9·800†					
$CeOs_2Si_2$	4·160	9·838	2·364	170·25	—	—	—
	4·160†	9·843†					
$YbPd_2Si_2$	4·090	9·854	2·409	164·83	—	30	—
$YbPd_2Ge_{0.05}Si_{1.95}$	4·091	9·868	2·412	165·15	—	—	—
$YbPd_2Ge_{0.1}Si_{1.9}$	4·098	9·864	2·407	165·65	—	45	—
$YbPd_2Ge_{0.3}Si_{1.7}$	4·107	9·873	2·404	166·53	—	70	—

† Hiebl *et al* (1984); †† Felner and Nowik 1985

in $CeRu_2Si_2$ increases the susceptibility at all temperatures whereas deficiency of ruthenium generates exactly the opposite effect (figure 2), carbon substitution, as shown in figure 3, decreases susceptibility which is consistent with what one should expect. Germanium-doped material $CeRu_2Si_{2-x}Ge_x$ exhibits a variety of magnetic behaviour, initially with small x (0·1), Ce moment becomes more stable. With 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 an 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 $\chi(T)$ vs T plot but also from the magnetization of the sample measured as a function of the applied field H ($0 > H > 8$ kilogauss), shown in figure 4. The material $CeRu_2SiGe$ exhibits a rather complex behaviour in that $\chi(T)$ of this system shows a peak at 9 K, just as in an antiferromagnet, and increases again at still lower temperatures. Magnetization behaviour also is not simple. It is not clear whether the peak at 9 K corresponds to a spin glass freezing which at lower temperature gives way to yet another type of magnetic ordering. Further experiments are underway to clarify the magnetic behaviour of this composition.

The germanium substitution brings about a completely opposite effect in $YbPd_2Si_2$ as compared to $CeRu_2Si_2$ system. The high temperature susceptibility of $YbPd_2Si_2$ is consistent with ytterbium being essentially trivalent (at high temperature). However, as pointed out earlier the susceptibility peaks at ~ 30 K and the material does not

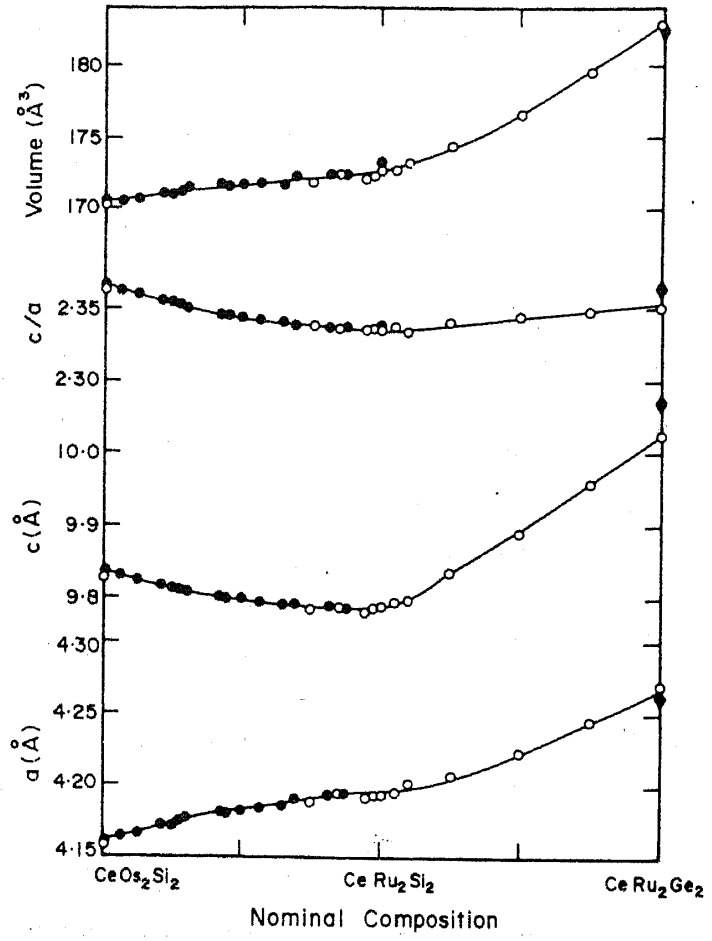

Figure 1. Variation of the lattice parameters a and c, the a/c ratio and unit cell volume for $CeRu_{2-x}Os_xSi_2$ and $CeRu_2Si_{2-x}Ge_x$ (O present work, ● Hiebl *et al* 1984, ■ Felner *et al* 1985).

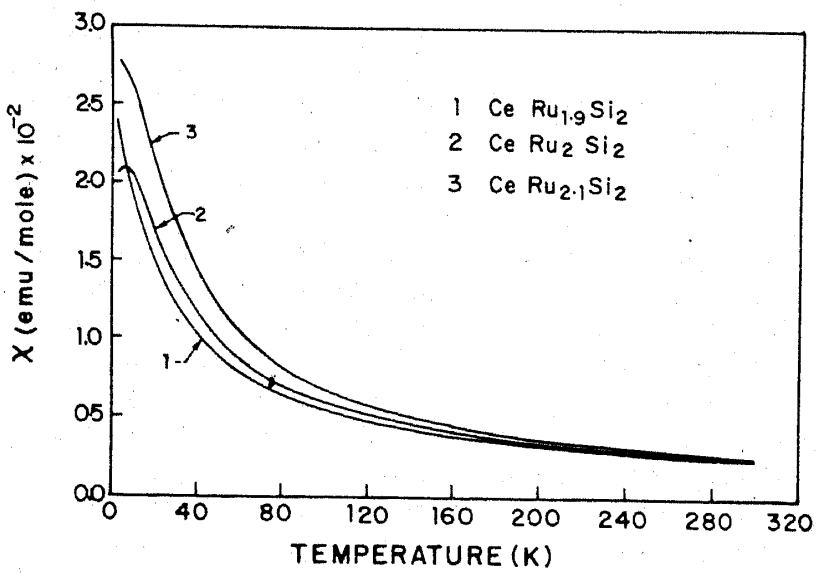

Figure 2. Susceptibility versus temperature for $CeRu_xSi_2$.

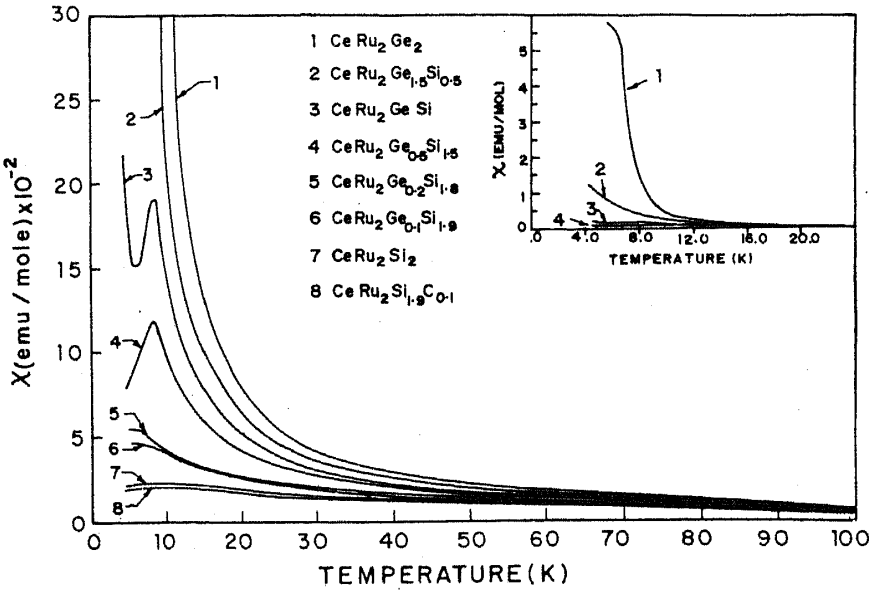

Figure 3. Susceptibility versus temperature for C and Ge substituted $CeRu_2Si_2$. Inset shows low temperature data for magnetic Ge substituted samples.

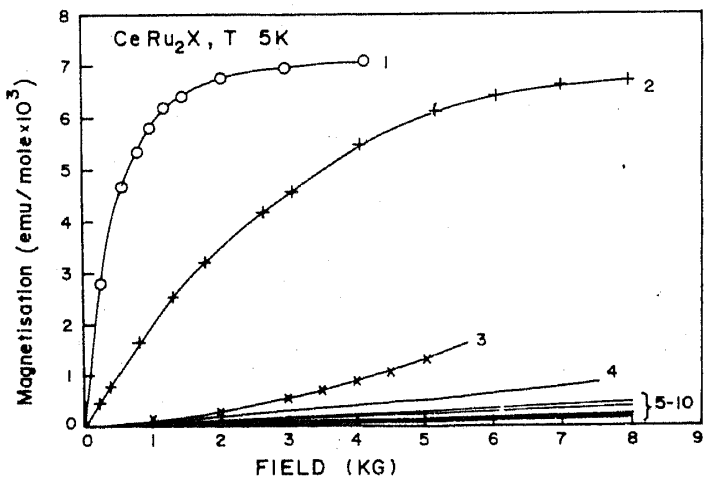

Figure 4. Magnetization versus field for C and Ge substituted $CeRu_2Si_{2-x}X_x$ (X_x = Ge_2(1); $Ge_{1.5}$(2); Ge(3); $Ge_{0.5}$(4); $Ge_{0.2}$(5); $Ge_{0.1}$(6) and $C_{0.1}$(10) and $CeRu_xSi_2$ (x = 2·1 (7); 2(8); 1·9(9))

undergo magnetic phase transitions at low temperature. On germanium substitution, the susceptibility decreases and the maximum in susceptibility gets shifted to a higher temperature. For instance, the maximum in $\chi(T)$ occurs at $\sim$ 30 K for $x = 0$ and 60 K for $x = 0{\cdot}3$. This suggests that valence of Yb becomes more unstable due to the increased size of the lattice induced by the presence of germanium. Some of the Yb samples showed an up turn in $\chi(T)$ at low temperature ($T > 8$ K) due to the presence of Yb^{3+} impurity. This low temperature tail in susceptibility was subtracted from the data for further analysis.

Magnetic susceptibility, as a function of temperature, measured on osmium substituted samples $CeRu_{2-x}Os_xSi_2$ is displayed in figure 5. It is clear from the figure

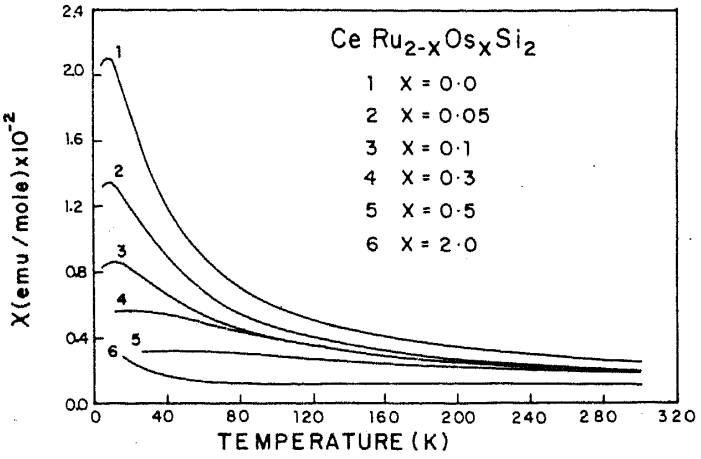

Figure 5. Susceptibility versus temperature for $CeRu_{2-x}Os_xSi_2$.

that with increasing x, the susceptibility decreases. Though the metallic radii of Ru and Os are very similar ($r_{Ru} \simeq 1{\cdot}34$ A and $r_{Os} \simeq 1{\cdot}35$ A), 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 $x = 0{\cdot}1$ and $T(\chi_{max}) = 25$ K for $x = 0{\cdot}3$. Susceptibility of full osmium sample does not show a clear maximum which is in agreement with the results of Hieble *et al* (1984).

4. Discussion

In Kondo lattice systems, magnetic susceptibility is described in terms of T_{sf}, the spin fluctuation temperature, which is defined as

$$T_{sf} = (C/2)\chi(0),$$

where C is the Curie constant for free ions (in this case Ce^{3+} ions) and $\chi(0)$ is the $\chi(T)$ of the system at $T = 0$ K. Alternatively spin fluctuation temperature T_{sf}^* is also defined (Lawrence 1979) as the temperature such that

$$T\chi(T)/C = 1/2.$$

Table 1 shows the values of T_{sf} and T_{sf}^* obtained using both 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 $CeRu_{2\cdot1}Si_2$ and $CeRu_{1\cdot9}Si_2$, it follows that excess (deficiency) of ruthenium decreases (increases) T_{sf} in $CeRu_2Si_2$. It is instructive to compare this behaviour 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 $CeCu_2Si_2$ (Spille *et al* 1983).

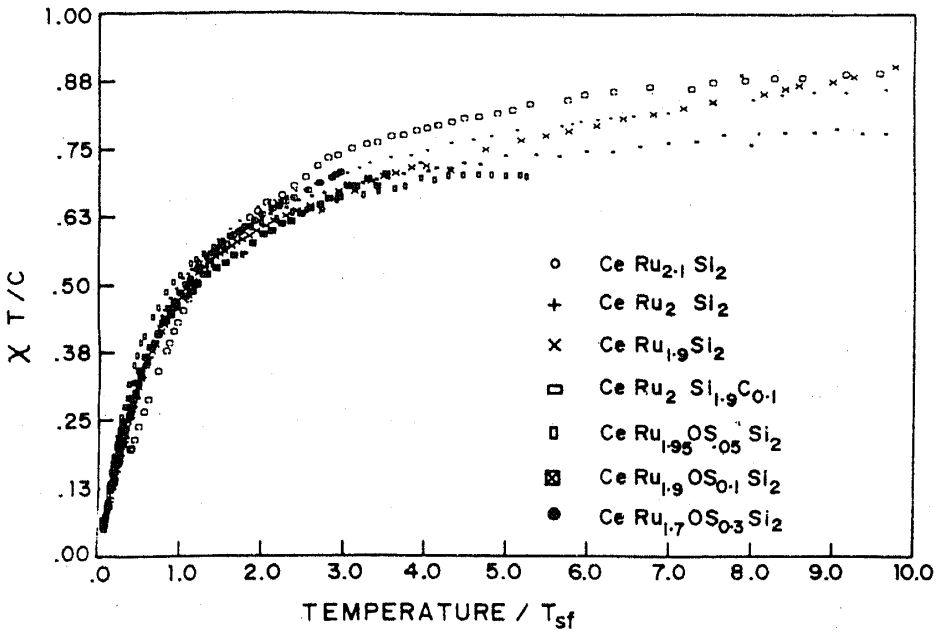

Figure 6. $\chi T/C$ versus T/T_{sf}^* for mixed valent pseudoternary $CeRu_2Si_2$ (see text).

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 that of Fermi liquid (Lawrence 1979). The magnetic susceptibility of such materials obeys a scaling behaviour 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 temperature, is not too big and the system stays non-magnetic at low temperature. Such a behaviour has been observed earlier (Lawrence 1979) 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 $T\chi(T)/C$ vs T/T_{sf}^* for many materials studied here. The scaling behaviour is roughly valid. The scatter that one sees at high temperatures in some cases is because of two reasons: Firstly we have not subtracted 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 $T\chi(T)/C$ vs $\ln T/T_{sf}^*$ rather than plotting $T\chi(T)/C$ vs T/T_{sf}^*. This procedure has a smoothening effect due to which the data apparently seem to follow the universal behaviour rather closely. Values of T_{sf}^* for various compositions obtained in our work are given in table 1.

It is instructive to examine the first *nn* environment of Ce in $CeRu_2Si_2$ and $CeOs_2Si_2$. There are 8 TM(Ru,Os) neighbours at a distance of $[(a/2)^2 + (c/4)^2]^{\frac{1}{2}}$ Å and 8 Si neighbours at a distance of $[(a^2/2) + c^2(1/2 - z)^2]^{\frac{1}{2}}$ Å. The variable parameter z has to be determined experimentally, either by a single crystal x-ray structural investigation or by EXAFS and is therefore not available generally. For these two materials, however, values of z have been determined by single crystal work; $z = 0{\cdot}365$ for $CeRu_2Si_2$ (Godart *et al* 1986) and $z = 0{\cdot}371$ for $CeOs_2Si_2$ (Horvath and Rogl 1983). Using these values of z, one can calculate Ce-Si and Ce-TM in these two materials. They are as:

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. The Ce-Si distance in $CeOs_2Si_2$ is ~ 1·5 % shorter than that in $CeRu_2Si_2$ and Ce-Ru is very nearly equal to Ce-Os. Thus it is clear that $CeOs_2Si_2$, it is not the chemical pressure effect which is responsible for nearly 'tetravalent' state of Ce. There is an increased overlap between Ce and Si in $CeOs_2Si_2$ as compared to that in $CeRu_2Si_2$ which drives cerium towards tetravalence.

It should be noted that in both these materials, Ce-Ce distance is much larger than the Hill limit (Hill 1970) and therefore the direct overlap of 4*f*-wavefunctions located on different Ce atoms is not responsible for the delocalization of the 4*f*-electron or to express it equivalently, for the formation of narrow 4*f*-band. The delocalization essentially occurs through hybridization of the *f*-electron wave function with the *s*-, *p*-ord-wave functions of the neighbouring (in these cases 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 $\chi(0)$ also strongly suggests enhancement of γ. 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}) (Ott *et al* 1984) having a magnetic ground state are known. We have, therefore, undertaken a detailed investigation of the physical properties of $CeRu_2Si_{2-x}Ge_x$ 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 $CeRu_2Si_2$ and $YbPd_2Si_2$ has been investigated. It is concluded that nearly 'tetravalent' character of Ce in $CeOs_2Si_2$ vis-a-vis nearly trivalent character of Ce in $CeRu_2Si_2$, is due to the increased overlap of Ce 4*f*-wavefunction with silicon wavefunctions. $CeRu_2Si_{2-x}Ge_x$ exhibits a most interesting behaviour in that with small concentrations of Ge, magnetic susceptibility increases without the system becoming magnetically ordered. This indicates that γ also should get enhanced. Possibility and implications of $CeRu_2Si_{2-x}Ge_x$ (with a certain value of x) being a heavy fermion with a magnetic ground state have been pointed out. Substitution of Si by Ge in $YbPd_2Si_2$ reduces the magnitude of susceptibility maximum χ_m at low temperature and also shifts χ_m towards high temperature. Both of these observations suggest that spin fluctuation temperature T_{sf} increases with the increase of Ge-concentration.

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