# Investigation of the magnetic-non-magnetic crossover region in the Kondo lattice system $CeSi_x$

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# Investigation of the magnetic–non-magnetic crossover region in the Kondo lattice system $CeSi_x$

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**Abstract.** Measurements of resistivity, susceptibility and magnetization for polycrystalline samples of the alloys $CeSi_x$ ($1.6 \leqslant x \leqslant 2.00$) in the temperature range 4–300 K show that samples with $x \leqslant 1.85$ order ferromagnetically while those with $x \geqslant 1.90$ do not. This correlates well with previous studies of these samples. However, samples with $x = 1.70$ and 1.75 show the presence of an anomalous second peak at a slightly higher temperature than the ferromagnetic ordering temperature. $CeSi_x$ with $x = 1.90$ shows interesting resistive behaviour with characteristics of both magnetic and non-magnetic samples. It exhibits a broad low temperature peak, a Kondo minimum at higher temperatures and the onset of Fermi liquid behaviour below the maximum. The magnitude of the room temperature resistivity is substantially larger than that of the other members of the series, indicating that this sample is very close to the critical concentration for the magnetic–non-magnetic transition in this series. High temperature anomalies are seen in the resistivities of samples with $x \geqslant 1.90$; nonetheless, no magnetic correlation is observed. Negative magnetoresistance is observed for samples $CeSi_{1.70}$ and $CeSi_{1.90}$ over all fields and temperatures investigated.

## 1. Introduction

$CeSi_2$ is known to crystallize in the tetragonal $\alpha$-$ThSi_2$ structure. For alloys of the series $CeSi_x$ ($1.00 \leqslant x \leqslant 2.00$) a decrease in Si concentration results first in Si vacancies within this structure, then, for $x \leqslant 1.75$, in a crystallographic distortion, and the alloys have the orthorhombic $GdSi_2$-type structure (Lee *et al* 1987). Alloys with $x \leqslant 1.60$ are multiphase (Pierre *et al* 1990). Variations in Si concentration also affect the electrical and magnetic properties of these alloys. Alloys of the series $CeSi_x$ with $x \leqslant 1.85$ are found to order magnetically, while those of $x \geqslant 1.90$ do not (Gschneidner *et al* 1989). Lee *et al* (1987) found that for $1.65 \leqslant x \leqslant 1.80$ $T_c$, the ferromagnetic ordering temperature remains constant at 13 K, while for higher concentrations of Si, $T_c$ decreases rapidly with increasing $x$.

Magnetization measurements by Yashima *et al* (1982) have shown that the magnetic moment per Ce atom in the ordered state is greatly reduced and specific heat measurements show reduced magnetic entropy below $T_c$. These experimental results led them to propose that the magnetically ordered state may be understood in terms of a ferromagnetic dense Kondo system, where a regular sublattice of Ce ions orders magnetically via the RKKY interaction, while the Kondo effect reduces the magnetic moment per ion.

The series of compounds $\mathrm{CeSi}_x$ is interesting and important because it is one of the few Kondo lattice compounds that orders ferromagnetically. A transition from a non-ordered magnetic state to a ferromagnetically ordered state is observed as silicon content is decreased, in contrast to the more familiar method of adding a non-magnetic third element which would complicate the analyses of experimental results. The nature of the transition from a well ordered ferromagnetic state to a state showing lack of magnetic ordering with variation in silicon content prompted us to undertake magnetic and electrical measurements on this series of compounds. In this communication we would like to present the results of resistivity, DC magnetization, AC susceptibility and magnetoresistance studies of polycrystalline samples of $\mathrm{CeSi}_x$ for $1.60 \leqslant x \leqslant 2.00$.

## 2. Experimental details

$\mathrm{CeSi}_x$ samples for $1.60 \leqslant x \leqslant 2.00$ in increments of 0.05 were prepared by mixing appropriate amounts of Ce (99.9%) and Si (99.999%) and arc melting them several times in an Ar atmosphere to ensure homogeneity. Samples were then annealed at 950 °C for seven days under $10^{-5}$ to $10^{-6}$ Torr pressure. Sample weight was monitored at each stage of preparation. However, due to silicon loss during arc melting it is likely that true silicon concentrations are up to several percent lower than reported here. Analysis of x-ray diffraction data for samples with $x = 1.90$ and $x = 1.70$ showed that both of these samples are single phase.

Resistivity was measured in the temperature range 4.2 to 290 K by the standard four-probe method using a constant DC current of 10 mA. AC susceptibility was measured using the mutual induction method in a field of approximately 1.3 Oe at 80 Hz over the same temperature range. Magnetization measurements were made using a SQUID magnetometer. Magnetoresistance at various temperatures was measured by the four-probe method both longitudinally and transversely to the magnetic field. Resistance was measured at each temperature in fields from 0 to 55 kG and back. Samples were warmed to above 20 K (above $T_c$) between field scans. Low field magnetoresistance below 4 K was measured in the SQUID magnetometer.

## 3. Experimental results

Samples of $\mathrm{CeSi}_x$ for $1.60 \leqslant x \leqslant 1.85$ were found to order ferromagnetically at low temperatures, while those with $x \geqslant 1.90$ do not (figure 1). In figure 1 it can also be seen that the magnetic moment of the Ce ion increases with Si concentration until $x = 1.80$, then is reduced greatly for $x = 1.85$ ($\mu_s = 0.1\mu_B$ per Ce). Magnetization measurements show that for samples with $x = 1.60$ and $x = 1.65$ $T_c$ remains constant at 10.6 K, increases to 12.1 K at $x = 1.80$, then decreases rapidly with increasing $x$ (figure 2).

A second magnetic transition, occurring at a temperature slightly higher than the ferromagnetic transition temperature, shows up clearly for $x = 1.70$ (figure 3) and 1.75 of our polycrystalline samples; it is not observed in any of the other members of the series. This second transition has only been observed previously in single crystals of Si concentration $x = 1.70$ (Sato et al 1988) and 1.71 (Pierre et al 1990). AC susceptibility measurements clearly show the ferromagnetic transition for samples of

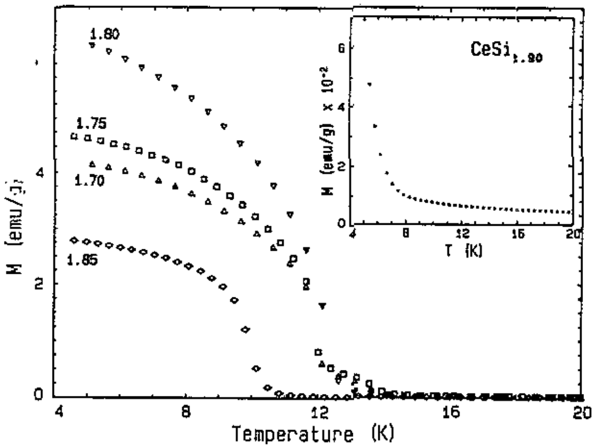

**Figure 1.** Magnetization ($M$) as a function of temperature from 4 to 24 K for CeSi$_x$ ($1.70 \leqslant x \leqslant 1.90$) in a magnetic field of 100 Oe. Curves correspond to $x = 1.70$ ($\Delta$), $x = 1.75$ ($\square$), $x = 1.80$ ($\nabla$), $x = 1.85$ ($\Diamond$) and $x = 1.90$ (see inset).

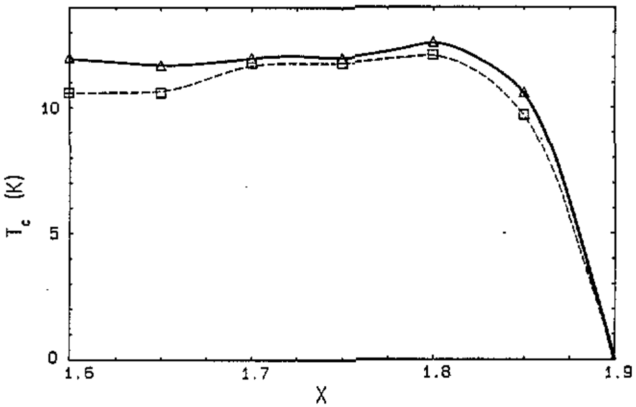

**Figure 2.** Ferromagnetic ordering temperature as a function of concentration for CeSi$_x$ ($1.60 \leqslant x \leqslant 1.85$), as determined from resistivity measurements ($\Delta$), and magnetization (SQUID) measurements ($\square$). (Lines are a guide to the eye.) Samples with $x \geqslant 1.90$ show no magnetic transition.

Si concentration $x \leqslant 1.85$ and also confirm the second transition at slightly higher temperatures for $x = 1.70$ (figure 3(*b*)) and 1.75.

Results for resistivity measurements are presented in figure 4. For samples with $x \leqslant 1.85$ the data show a low temperature peak which corresponds to $T_c$. Samples with $x = 1.70$ and 1.75 show evidence of the second transition at a temperature slightly higher than $T_c$ (see inset to figure 3(*b*)) which correlates well with the magnetization data. Above $T_c$, resistivity decreases slowly to a broad minimum at 200 to 250 K, then rises again as room temperature is approached. Below $T_c$ resistivity drops sharply. Alloys with $x \geqslant 1.95$ show a continuously increasing resistivity from 4.2 to 290 K. High temperature anomalies similar to those observed by Gschneidner *et al* (1989) for polycrystalline samples and by Pierre *et al* (1990) for single crystals with $x = 1.71$ and 1.86 are seen in our samples at 240 K for CeSi$_{1.95}$ and at 210 K for

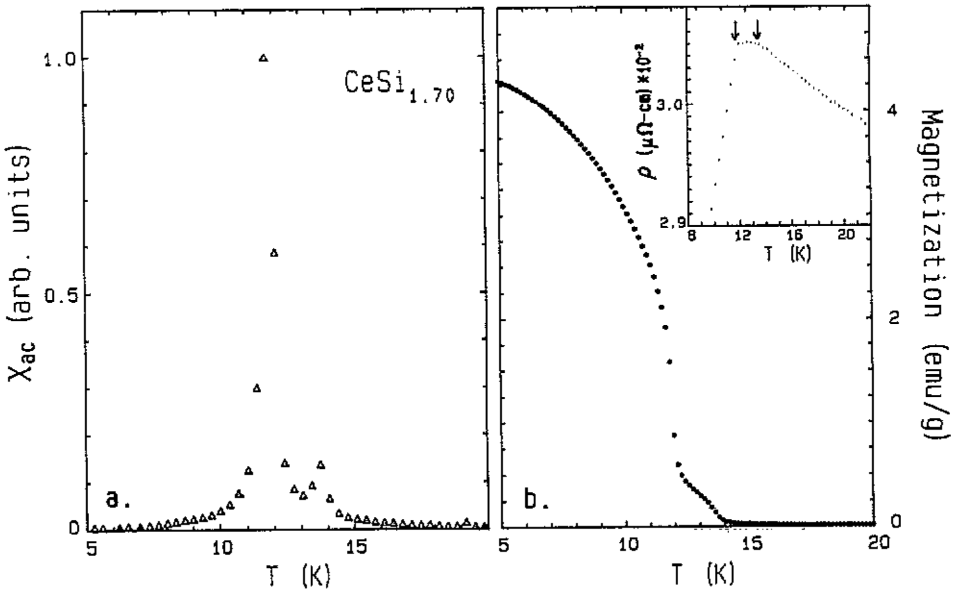

**Figure 3.** (*a*) AC susceptibility ($\chi_{AC}$), normalized to peak value, for $CeSi_{1.70}$ showing the presence of the ferromagnetic transition and an anomalous second transition at a slightly higher temperature. Our sample with $x = 1.75$ shows similar behaviour. (*b*) Magnetization ($M$) as a function of temperature for $CeSi_{1.70}$ showing the presence of a second magnetic transition at a temperature slightly higher that $T_c$. Inset shows the behaviour of the resistivity over the same temperature range. Our sample with $x = 1.75$ shows similar behaviour.

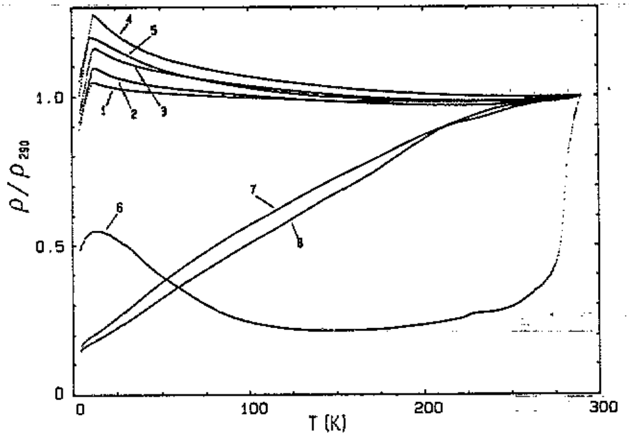

**Figure 4.** Electrical resistivity normalized to the value at room temperature ($\rho/\rho_{290}$) as a function of temperature for alloys in the system $CeSi_x$: (1) $x = 1.65$; (2) $x = 1.70$; (3) $x = 1.75$; (4) $x = 1.80$; (5) $x = 1.85$; (6) $x = 1.90$; (7) $x = 1.95$; (8) $x = 2.00$.

$CeSi_{2.00}$. No magnetic correlation is observed for these anomalies and their nature is not well understood at present.

Our sample with Si concentration $x = 1.90$ shows interesting resistive behaviour (figure 4) with characteristics intermediate to those of the magnetic and non-magnetic samples. Resistance rises to a broad peak at 13 K then decreases to a broad minimum centred near 150 K. Resistivity then rises as temperature is increased. A high temperature anomaly is seen at 228 K and there is a large increase in resistivity near 280 K. Except for the appearance of the high temperature anomaly and abrupt increase in resistivity near 280 K, the resistivity curve of $CeSi_{1.90}$ is qualitatively similar to those of the typical Kondo lattice systems $CeAl_3$ (Edelstein *et al* 1977) and $CeCu_6$ (Sumiyama *et al* 1986).

The sharp drop in resistivity below $T_c$ for the magnetically ordered samples, and below the broad low temperature maximum in $CeSi_{1.90}$, may be associated with coherent scattering from the Ce ions and the onset of Fermi liquid behaviour at low temperature. Fermi liquid theory predicts a $T^2$ dependence of resistivity at low temperatures. Our samples with $x \leqslant 1.85$ show a nearly linear temperature dependence from the ferromagnetic transition temperature down to 5 K. Further measurements down to 1.8 K on the magnetically ordered sample $CeSi_{1.85}$ (figure 5(*a*)) show a $T^2$ temperature dependence between 1.8 and 4.2 K, with the coefficient $A = 1.487$ $\mu\Omega$ cm $K^{-2}$. For members of the series that do not order magnetically, resistivity at low temperatures shows a positive curvature. Even measurements on $CeSi_{1.90}$ down to 1.8 K (figure 5(*b*)) show this positive curvature.

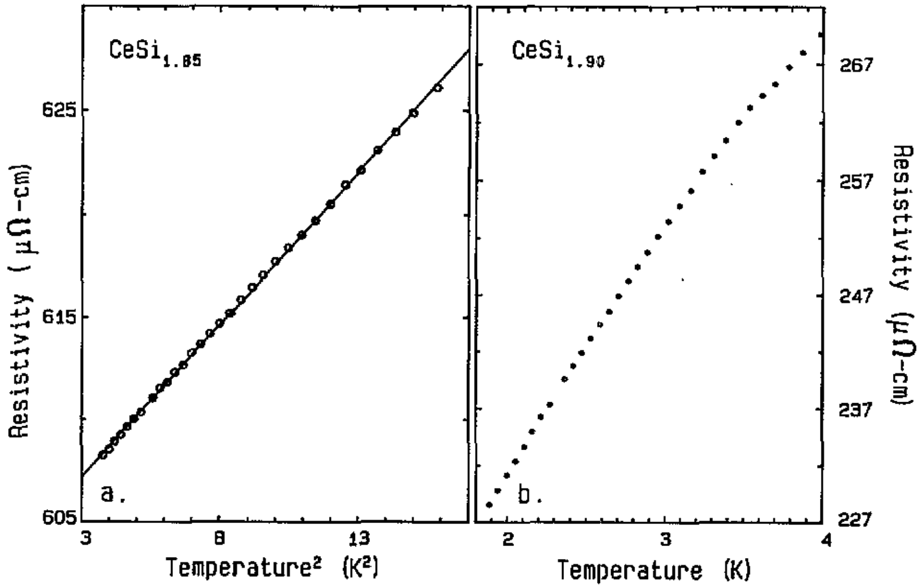

**Figure 5.** (*a*) Resistivity as a function of temperature below 4.2 K for $CeSi_{1.85}$ showing a linear $T^2$ dependence. The slope was calculated as $A = 1.487$ $\mu\Omega$ cm $K^{-2}$. (*b*) Resistivity as a function of temperature below 4.2 K for $CeSi_{1.90}$ showing a slight positive curvature.

Another interesting feature of the resistance curve for $x = 1.90$ is the magnitude of the room temperature resistance, which is more than a factor of 100 greater than any of the other members of the series. The others vary from each other by no more than a factor of three.

Subsequent resistivity measurements to verify these behaviours were made on other samples cut from the same ingot. Room temperature values of resistivity on two later runs were more nearly in line with the other members of the series, one being a factor of ten larger, the other being of the same order of magnitude as

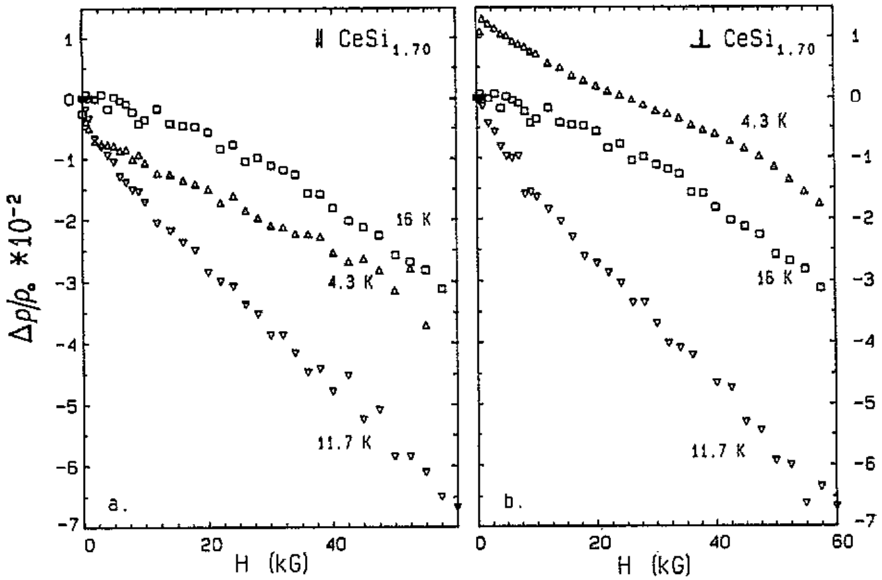

**Figure 6.** (*a*) Longitudinal and (*b*) transverse magnetoresistance as a function of field for $CeSi_{1.70}$ at several temperatures. (The initial rise in magnetoresistance for $T$ = 4.3 K is most likely an experimental artifact.)

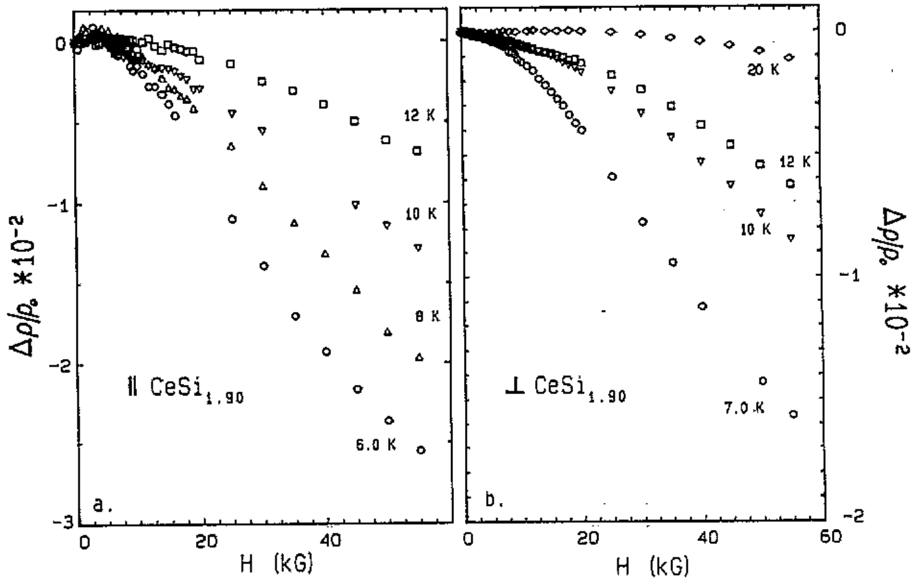

**Figure 7.** (*a*) Longitudinal and (*b*) transverse magnetoresistance as a function of field for $CeSi_{1.90}$ at several temperatures.

the other members of the series. Despite the discrepancies in the magnitude of the room temperature resistivity, all resistivity measurements on $CeSi_{1.90}$ have several characteristics in common; all three samples cut from our $x$ = 1.90 ingot show a broad rounded peak at low temperatures, the maximum occurring at temperatures of 13, 39 and 37 K; below these temperatures the resistance drops rapidly; all three samples show a broad Kondo minimum at about 150, 175 and 200 K, respectively; finally, all three samples show small anomalies near 230 K and a rapid increase in resistivity near 280 K. The broad peak at low temperature together with the Kondo minimum at higher temperatures and the onset of coherence below the peak show that this sample is remarkably similar to the Kondo lattice compounds $CeAl_3$ and $CeCu_6$. The similarity in the resistive behaviours of the three Kondo lattice compounds $CeAl_3$, $CeCu_6$ and $CeSi_{1.90}$ motivated us to undertake low temperature, low field magnetoresistance measurements on the latter.

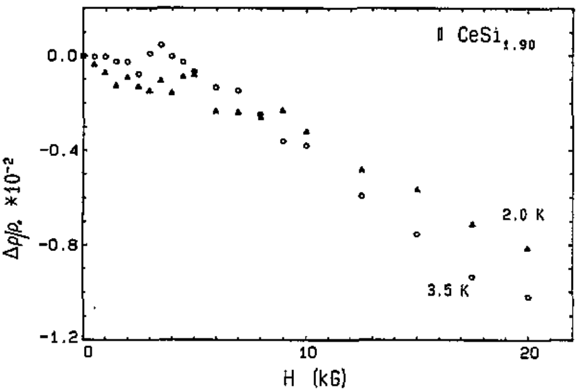

**Figure 8.** Longitudinal low temperature low field magnetoresistance of $CeSi_{1.90}$.

Transverse and longitudinal magnetoresistance measurements on samples with $x = 1.70$ and 1.90 at various temperatures and for increasing field are shown in figures 6 and 7. $CeSi_{1.70}$ (figure 6(*a*),(*b*)) shows a negative magnetoresistance for all temperatures measured, both above and below the ordering temperature. The magnetoresistance shows no tendency to saturate in fields of up to 55 kG. The largest magnitude of the magnetoresistance is observed at 11.7 K, very close to $T_c$ for this sample.

The transverse and longitudinal magnetoresistance for our sample $CeSi_{1.90}$ (which shows no evidence of magnetic ordering down to 4.2 K) also shows negative magnetoresistance for all temperatures measured. The behaviour of this sample is similar to the low field transverse *c*-axis magnetoresistance data on single crystal $CeSi_{1.86}$ measured by Laborde *et al* (1990). Additional longitudinal magnetoresistance measurements below 4.2 K on this sample are presented in figure 8. The largest magnitude of the magnetoresistance for this sample occurs for $T = 3.5$ K.

## 4. Discussion

Magnetic and electrical measurements on members of the series $CeSi_x$ support the Kondo lattice description of these compounds. The resistivity minimum seen in the magnetically ordered members of the system and in $CeSi_{1.90}$ can be explained in terms of the Kondo effect. Plots of resistivity versus $\ln(T)$ (not shown here) for the magnetic samples are consistent with the findings of Yashima *et al* (1982) which show that the Kondo temperature, $T_K$, increases with increasing silicon content. Recent neutron scattering experiments (Galera *et al* 1989, and references therein) have found $T_K$ for $CeSi_{1.85}$ and $CeSi_{2.0}$ to be 20 K and 41 K, respectively.

Our sample with $x = 1.90$ does not order magnetically, but exhibits behaviours, such as the large value of room temperature resistivity, that indicate that it is very close in composition to the critical magnetic–non-magnetic crossover point. Resistivity measurements by Gschneidner *et al* (1989) show room temperature resistivities to rise sharply in the immediate vicinity of the magnetic–non-magnetic crossover point of the series. They note a sharp increase of nearly an order of magnitude extending over a very small concentration range, roughly 0.2 atomic percent, very close to the critical concentration of $x = 1.855$. The peak in resistivity versus Si concentration ($x = 1.90$, for our samples) corresponds to the concentration for $T_c = 0$ K, the composition at which the material goes from a non-magnetic spin fluctuator ground state (delocalized 4f electrons), to a ferromagnetic ground state (localized 4f electrons). They suggest that this large resistivity near the critical concentration is due to the Ce ion being driven from the delocalized low-volume state to the localized large-volume state upon warming. Upon warming the Ce ion tends to expand and the rigid Si network relieves the stress by forming cracks.

Even though the resistivity of $CeSi_{1.90}$ does not show a $T^2$ dependence at low temperatures, as predicted by Fermi liquid theory, this low temperature resistivity behaviour for a Kondo lattice compound may be reconciled with the fact that in many cases, for example $CeAl_3$, $CeCu_2Si_2$, $CeB_6$ and $CeCu_6$, the $T^2$ dependence for Fermi liquid systems is seen only below 1.0 K (Sumiyama *et al* 1986, and references therein). Also, in some cases there appears to be a linear approach to coherence (Sumiyama *et al* 1986).

$CeAl_3$ and $CeCu_6$ are two Kondo lattice compounds with non-magnetic ground states which appear to be close to some sort of magnetic instability, as is $CeSi_{1.90}$. All three show remarkably similar behaviour in their resistivity as a function of temperature. All three show evidence of Kondo scattering at high temperatures followed by a broad low temperature peak below which resistivity drops rapidly, indicating the onset of coherence and Fermi liquid behaviour. A major difference, however, between $CeSi_{1.90}$ and the other two compounds is that $CeSi_{1.90}$ has a significantly higher Kondo temperature than either $CeAl_3$ ($T_K = 5$ K) or $CeCu_6$ ($T_K = 3$ K.)

Another feature in the resistivity behaviour of both $CeAl_3$ and $CeCu_6$, and thought to be a general feature of Kondo lattice compounds, is the appearance of a positive peak in magnetoresistance for low fields at sufficiently low temperatures. According to Kawakami and Okiji (1986) the onset of positive magnetoresistance scales with the Kondo temperature and may be attributed to the gap structure of the Kondo resonance slightly above the Fermi level. $CeAl_3$ has a Kondo temperature of 5 K and shows the onset of positive magnetoresistance at low fields (peak at approximately 20 kG) for $T \leqslant 1.0$ K (Remenyi *et al* 1983). Similarly, $CeCu_6$, with a Kondo temperature of 3 K, shows the onset of positive low field magnetoresistance (peak at approximately 20 kG) for $T \approx 0.55$ K. Since both $CeAl_3$ and $CeCu_6$ show the onset of positive magnetoresistance at $T/T_K \approx 0.2$ it is quite plausible that $CeSi_{1.90}$ should show the same effect for $T/T_K \approx 0.2$. With the estimated Kondo temperature for 20 K this gives a value of $T = 4.0$ K, thus a positive low field magnetoresistance might be expected for temperatures at and below 4.0 K. However, no positive magnetoresistance is observed for this sample even at temperatures as low as 2.0 K.

$CeCu_6$ and $CeAl_3$ show a negative maximum in magnetoresistance for temperatures of 1.3 K (Sumiyama *et al* 1985) and about 1.2 K (Remenyi *et al* 1983) as a precursor to the onset of positive low field magnetoresistance. $CeSi_{1.90}$ shows a negative maximum near 3.5 K, thus $CeSi_{1.90}$ may yet show positive low field magnetoresistance at sufficiently low temperatures.

## 5. Summary

In summary, samples of $CeSi_x$ with $1.6\text{-} \leqslant x \leqslant 1.85$ order magnetically at low temperatures. Samples with $x \geqslant 1.90$ show no magnetic order. Our polycrystalline samples with $x = 1.70$ and 1.75 clearly show the presence of a second transition at a temperature slightly higher than $T_c$, which has previously been observed only in single crystals of $x = 1.70$ and 1.71. There is no evidence of this second transition for other members of the series, thus it does not appear to be a characteristic of all the magnetic samples, but just those within a limited concentration range having the orthorhombic structure near the orthorhombic–tetragonal transition. The nature of this second transition is not understood at present.

Our sample with $x = 1.90$ has a room temperature resistivity much larger than the other members of the series, indicating that it is very close to the magnetic–non-magnetic crossover point for the series. It shows no magnetic transition but does have a broad peak in resistivity at low temperatures (between 13 K and 39 K for different samples) and a Kondo minimum at higher temperatures. There is also a sharp decrease in resistivity below the resistivity maximum indicating the onset of Fermi liquid behaviour at low temperature. The resistive behaviour of this sample is qualitatively similar to that of the Kondo lattice compounds $CeCu_6$ and $CeAl_3$. However, the positive low temperature magnetoresistance observed in $CeCu_6$ and $CeAl_3$ is not observed in our sample for temperatures down to 2 K. The magnetoresistance of $CeSi_{1.70}$ and $CeSi_{1.90}$ is negative for all fields and temperatures investigated.

## Acknowledgment

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## References

Edelstein A S, Majewski R E and Blewitt T H 1977 *Valence Instabilities and Related Narrow Band Phenomena* ed R D Parks (New York: Plenum) p 115

Galera R M, Murani A P and Pierre J P 1989 *Physica* B **156/157** 801

Gschneidner K A Jr, Lee W H, Damento M A, Tang J, Cook B A, Shinar J, Dehner B and Shelton R N 1989 *Phys. Rev.* B **39** 2099

Kawakami N and Okiji A 1986 *J. Phys. Soc. Japan* **55** 2114

Laborde O, Pierre J, Houssay E, Rouault A, Senateur J P and Madar R 1990 *J. Low Temp. Phys.* **81** 171

Lee W H, Shelton R N, Dhar S K and Gshneidner K A Jr 1987 *Phys. Rev.* B **35** 8523

Pierre J, Laborde O, Houssay E, Rouault A, Senateur J P and Madar R 1990 *J. Phys.: Condens. Matter* **2** 431

Remenyi G, Briggs A, Flouquet J, Laborde O and Lapierre F 1983 *J. Magn. Magn. Mater.* **31–34** 407

Sato N, Mori H, Satoh T, Miura T and Takei H 1988 *J. Phys. Soc. Japan* **57** 1384

Sumiyama A, Oda Y, Nagano H, Onuki Y and Komatsubara T 1985 *J. Phys. Soc. Japan* **54** 4470

Sumiyama A, Oda Y, Nagano H, Onuki Y, Shibutani K and Komatsubara T 1986 *J. Phys. Soc. Japan* **55** 1294

Yashima H, Mori H, Kohn K and Satoh T 1982 *Solid State Commun.* **43** 193