Title	Thermal and Magnetic Properties of Ce-Si System
Author(s)	Yashima, H.; Mori, H.; Satoh, T.
Citation	物性研究 (1982), 37(5): 42-48
Issue Date	1982-02-20
URL	http://hdl.handle.net/2433/90471
Right	
Type	Departmental Bulletin Paper
Textversion	publisher

Thermal and Magnetic Properties of Ce-Si System*

H. Yashima, H. Mori and T. Satoh

Department of Physics, Faculty of Science,
Tohoku University, Sendai, Japan

$CeSi_2$ and $CeGe_2$ are members of α-$ThSi_2$ type intermetallic compounds. The crystal structure is shown in Fig.1. This structure is known to be found only for silicides and germanides. Therefore it seems that the sublattice structure constructed by Si or Ge, which may be looked upon a 3-dimensional graphite structure, is important in forming this crystal structure.

In this note we wish to report tne results of our study in Ce-Si and Ce-Ge system. The lattice parameters measured at room temperature are a = b = 4.184A and c = 13.856A for $CeSi_2$ and a = 4.282A, b = 4.199A and c = 14.081A for $CeGe_2$. The measured specific heats are given in Fig.2 and Fig.3. The magnetic susceptibilities are shown in Fig.4.

From Fig.2 and Fig.4 we can see that $CeGe_2$ undergoes a magnetic transition at $T_c \simeq 7K$. Assuming Curie-Weiss law for the high temperature susceptibility, we obtain $\mu_{eff} = 2.41\mu_B$ which corresponds approximately to the magnetic moment of the free Ce^{3+} ion $\mu_{eff}(+3) = 2.56\mu_B$. Although the behavior of magnetic susceptibility near T_c suggests that the magnetically ordered state is ferromagnetic, the temperature dependence of specific heat below T_c can be fitted very well with T^3 law as shown in the inserted figure in Fig.2. The calculation of the entropy below T_c can be made with Fig.2 and gives the value of S = 5.74 J/mole·deg which is nearly equal to Rℓn2 where R is the gas constant. Neglecting the orthorhombic distortion in $CeGe_2$, the crystal field potential can be expressed as

$$V_c = A_o O_4 + A_1 J_z^4 + A_2 J_z^2 \quad . \qquad (1)$$

If we take into account up to the 4th nearest neighbor atoms and assume the charge at Ce site is +3 and that at the Ge site is zero, then we have a level scheme in which the ground state is a doublet $\sqrt{5/6} \mid \pm 5/2 > + \sqrt{1/6} \mid \mp 3/2 >$. Magnetization measurements were performed to give a saturation magnetization $M_s \simeq 0.86\mu_B$. Therefore it may be more reasonable to assign the ground state to be a Γ_7 doublet ($\sqrt{1/6} \mid \pm 5/2 > - \sqrt{5/6} \mid \mp 3/2>$) which gives $M_s \simeq 0.71\mu_B$.

For $CeSi_2$, as is clearly seen from Fig.3 and Fig.4, we do not see any phase transition in the investigated temperature range down to 100mK. The low temperature specific heat can be expressed very well by the equation

$$C = \gamma T + \beta T^3 \qquad (2)$$

with γ = 104 mj/mole·deg^2 and β = 0.211 mj/mole·deg^4 which corresponds to the Debye temperature $\Theta \simeq 302$K. It is noted the γ value obtained is almost 26 times larger than that of $LaGe_2$ or $LaSi_2$[1], whereas Θ is nearly the same. A simple fitting of the high temperature susceptibility with Curie-Weiss law gives $\mu_{eff}=3.14\mu_B$ which is much larger than $\mu_{eff}(+3)$. The finite ground state susceptibility is obtained by extrapolation as $\chi(0)=4.33\times10^{-3}$emu/mole. Thus the $\mathcal{R}$ ratio defined as

$$\mathcal{R} = \frac{\pi^2 k_B^2}{g^2 \mu_B^2 J(J+1)} \cdot \frac{\chi(0)}{\gamma} \qquad (3)$$

is calculated to give $\mathcal{R}$ = 1.41. The $\mathcal{R}$ ratio in the Kondo limit for Ce^{3+} is said to be $\mathcal{R} = (2J+1)/2J = 1.20$[2]. The low temperature susceptibility can be expressed very well with

$$\chi(T) = \chi(0) \quad (1+aT^2) \quad \text{for} \quad T < 25K \qquad (4)$$

$$a = -0.42 \times 10^{-3} \ (k^{-2})$$

as shown in Fig.4.

According to our previous study on La-Ge system[1], α-$ThSi_2$ type crystal structure is stable in a wide range of non-stoichiometric composition. Referring to the Si-sublattice structure shown in Fig.1(c), it would be expected that the deficiency of Si causes a change of the number of electrons in the conduction band. The intermediate valence state occurs due to the proximity of the 4f level to the Fermi energy level. Therefore it is interesting to see how the magnetic behavior found in $CeSi_2$ changes with Si deficiency.

The lattice parameters measured at room temperature are given in Tab.I. Although the lattice constants a, b and c vary with x, the unit cell volume does not show an appreciable change with x.

Magnetic susceptibilities were measured in the temperature range 4.2K to 300K. The results are shown in Fig.5. Specific heat measurements were made in the temperature region from 0.1K to 70K. The results are given in Fig.6 and Fig.7. From Fig.5, Fig.6 and Fig.7, we can summarize the main features of our results as follows.

(i) In the composition range $2.00 \geq \chi \geq 1.85$, $CeSi_x$ does not show any phase transition in the investigated temperature range down to 0.1K. The very-low temperature specific heat can be expressed very well by the equation

$$C = \gamma T \quad . \tag{5}$$

The value of γ is very large compared with that of $LaGe_2$ or $LaSi_2$ and it increases with decreasing x . The Fermi temperature is obtained from γ as

$$T_F(\gamma) = \frac{\pi^2 R}{2\gamma} \qquad R: \text{ gas constant} \quad . \tag{6}$$

Those values of γ and $T_F(\gamma)$ are listed in Tab.II.

(ii) For the samples of x = 2.00, 1.90 and 1.85, the finite ground state susceptibility $\chi(0)$ is obtained by extrapolation. The low temperature susceptibility can be expressed well with the equation

$$\chi(T) = \chi(0)(1+aT^2) \tag{7}$$

as shown in Fig.8. The sign of the T^2 term is negative for all samples. Those values of $\chi(0)$ and the coefficient a are given in Tab.II. The Fermi temperature estimated from $\chi(0)$ as

$$T_F(\chi) = \frac{3}{2}\frac{C}{\chi(0)} \quad , \qquad (C = 0.807 \text{ emuK/mole}) \tag{8}$$

are also listed in the same table.

(iii) For the composition $x \leq 1.85$ the system undergoes a sharp magnetic transition. The high temperature susceptibility can be fitted very well with the Curie-Weiss law

$$\chi = \frac{C'}{T+\Theta} \tag{9}$$

where C' = 0.768 emuK/mole which corresponds to $\mu_{eff} = 2.47\ \mu_B$.

(iv) As can be seen from Fig.5, the high temperature susceptibility of $CeSi_{1.90}$ and $CeSi_{1.85}$ can also be expressed with Eq.(9). In these cases Θ may be considered as a characteristic temperature determined by the strength of the s-f mixing interaction[3]. The values of Θ are listed in Tab.II.

(v) Below about 50K, all samples show a rather sharp increase of the magnetic susceptibility.

Above mentioned features (i) and (ii) suggest that Ce in $CeSi_x$ $x \leq 1.85$ is in the intermediate valence state and the ground state is a metallic Fermi liquid. The values of the parameter defined with Eq.(3) are given in Tab.II. As shown in Tab.II, $\mathcal{R}$ increases

rapidly near the critical composition. From the values of γ and $\chi(0)$ given in Tab.II, we can see that we have an approximate relation $\gamma \propto \ell n \chi(0)$ as in the case of a strongly exchange-enhanced paramagnon system[4]. Discussions of the present data based on the paramagnon model will be presented.

If the Fermi liquid-like behavior continues to exist also in the composition range of $x \leq 1.80$, it seems likely that the magnetically ordered phase might be a spin density wave state. The entropy below T_c can be calculated from the specific heat data and is given in Tab.II as ΔS. As can be seen ΔS is much smaller than $R\ell n2$. It is interesting to note that in the case of $CeGe_2$, ΔS is almost equal to $R\ell n2$, although the T_c is nearly the same as found in the present Ce-Si system.

Results on the ternary system $CeSi_{2-x}Ge_x$ will be given and the preliminary results of resistivity measurement will also be presented.

References

* A part of the present paper will appear in Solid State Communications. Thermal and Magnetic Properties and Crystal Structure of $CeGe_2$ and $CeSi_2$ by H. Yashima, T. Satoh, H. Mori, D. Watanabe and T. Ohtsuka, Nonmagnetic-Magnetic Transion in Ce-Si System by H. Yashima and T. Satoh.

1) T. Satoh and Y. Asada; J. Phys. Soc. Japan, 27 (1969) 1463. A Sawada and T. Satoh; J. of Low Temp. Phys. 30 (1978) 455.

2) D. M. Newns and A. C. Hewson; J. Phys. F. Metal Phys. 10 (1980) 2429.

3) C. M. Varma and Y. Yafet; Phys. Rev. 138 (1976) 1950.

4) J. R. Schriefer; J. Appl. Phys. 39 (1968) 642.

TABLE I.

	x = 2.00	x = 1.90	x = 1.85	x = 1.80	x = 1.70
a (Å)	4.278	4.192	4.170	4.170	4.168
b (Å)	4.278	4.192	4.170	4.170	4.098
c (Å)	13.646	13.692	13.722	13.729	13.815
a x b x c ($Å^3$)	249.74	240.61	238.61	238.73	235.97

TABLE II.

	γ $(\frac{mj}{mole \cdot K^2})$	$T_F(\gamma)$ (K)	$\chi(0)$ $(\frac{emu}{mole})$	$T_F(\chi)$ (K)	a x 10^3 (K^{-2})	$\mathcal{R}$	θ (K)	T_c (K)	ΔS $(\frac{J}{mole \cdot K})$
x = 2.00	104	390	4.2×10^{-3}	288	-0.42	1.41			
x = 1.90	151	271	7.0×10^{-3}	173	-0.55	1.62	101		
x = 1.85	234	175	4.0×10^{-2}	30	-2.7	6.04	76		
x = 1.80							42	9.0	3.41
x = 1.70							25	10.9	4.53

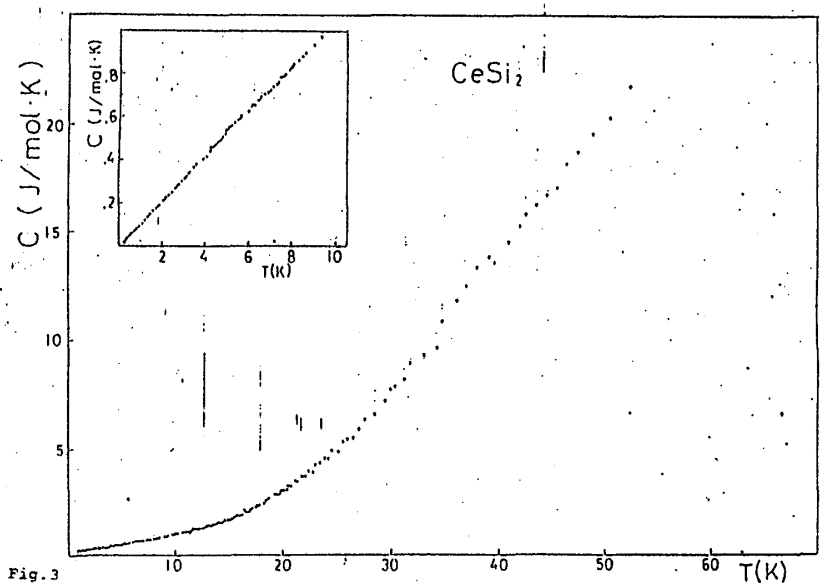

Fig.3

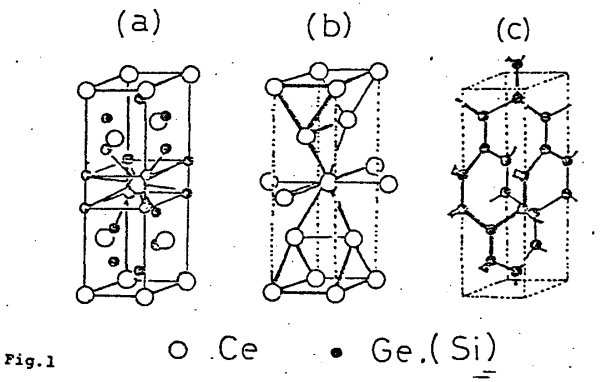

Fig.1

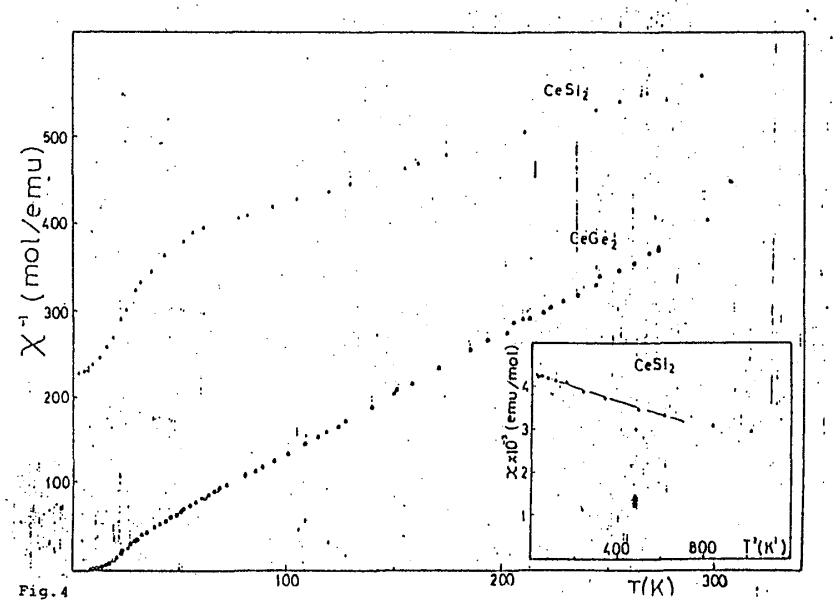

Fig.4

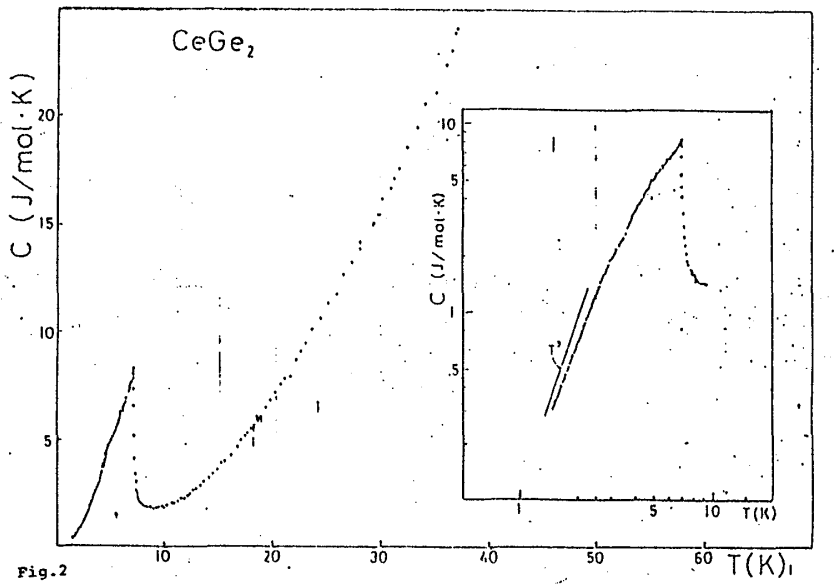

Fig.2

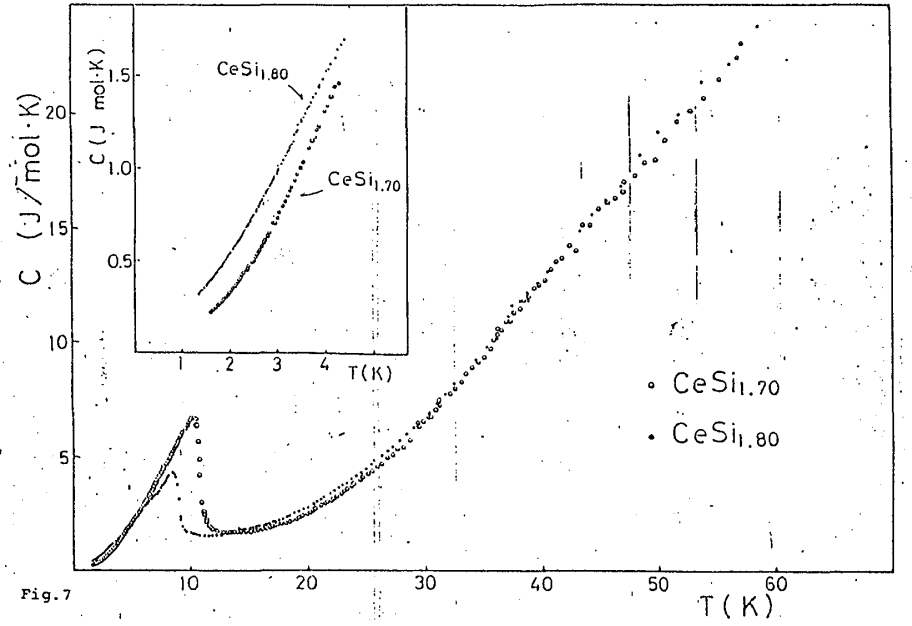

Fig.7

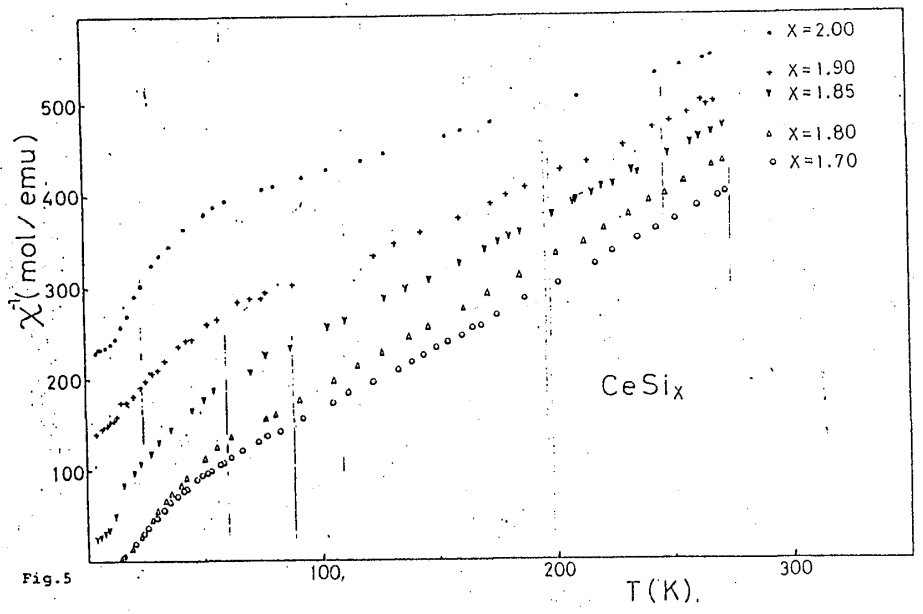

Fig.5

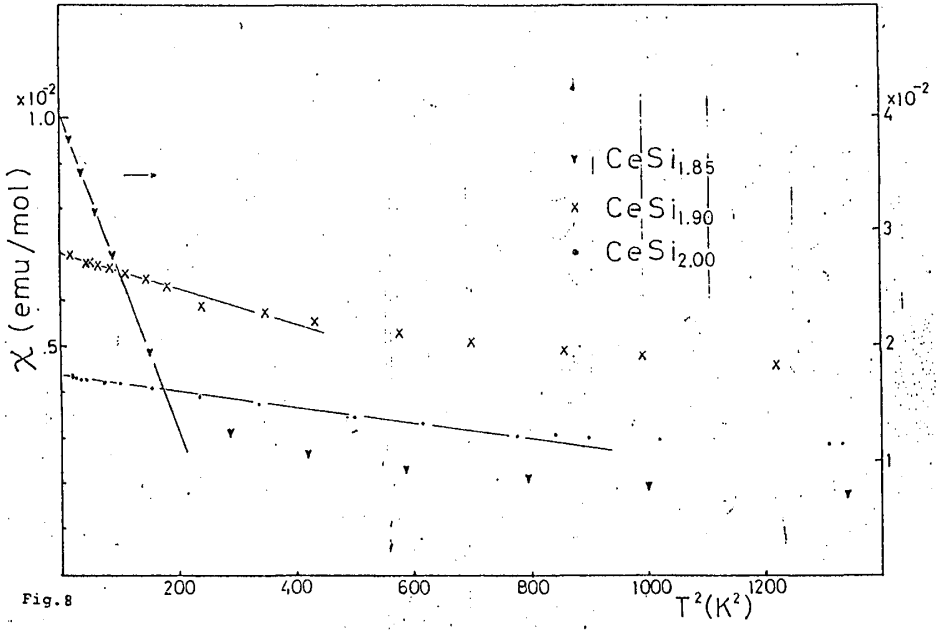

Fig.8

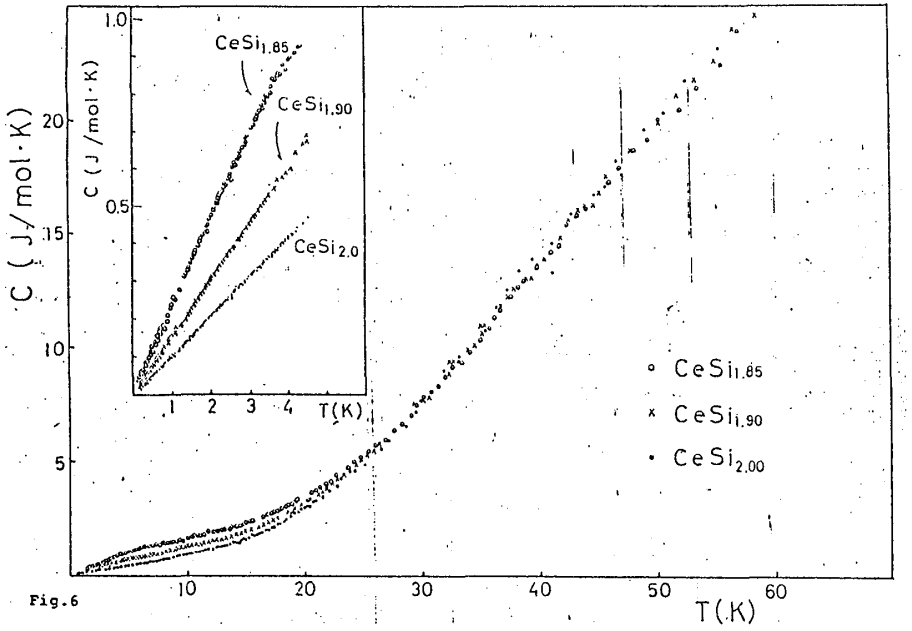

Fig.6