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CRYSTAL INSTABILITY IN CeSi$_x$

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In samples of CeSi$_x$ with $x \leqslant 2.00$ having a tetragonal α-ThSi$_2$ type crystal, an abnormal thermal contraction in addition to a crystal phase transition with a finite jump in lattice parameter c, keeping the same crystal structure, were observed. The instability of the crystal structure is discussed tentatively in term of its free energy.

CeSi$_x$ IS A system in which the Kondo type interaction and the RKKY type interaction are competing. CeSi$_{2.00}$ is an intermediate valence compound with a large Kondo temperature T_K, while CeSi$_x$ with $1.70 \leqslant x \leqslant 1.85$ is a ferromagnetic compound with T_C near 10 K and with its magnetic moment increasing with the decrease in x. On the other hand, CeSi$_x$ with $1.85 < x \leqslant 1.90$, the value of x between above the two cases, has a low T_K with an enhanced electronic specific heat coefficient [1, 2].

The crystal structure of CeSi$_{2.00}$ is known to be of a tetragonal α-ThSi$_2$ type shown in Fig. 1 [1]. In the present report, we show the results of our study of the crystal structure and lattice parameters for CeSi$_x$ as the function of x and as the function of the temperature. Complicated and interesting features of instability of the crystal structure were found.

We have prepared the five samples of CeSi$_x$ with x = 2.00, 1.90, 1.85, 1.80 and 1.70 by fusing the constituent elements in a plasma furnace under an Ar atmosphere and by subsequent annealing at 950°C in an evacuated quartz tube for a week. The purity of the original elements was 99.9% for Ce and 99.99% for Si, respectively. X-ray powder diffraction was carried out in a temperature range from 10 to 273 K with a low temperature cryostat having a liquid He reservoir. With a heater in the cryostat and with a temperature controller, a desired temperature was maintained within ± 1 K during the measurement of diffraction diagram.

The lattice parameters were obtained by the Nelson–Riley extrapolation formula of the Bragg angles 2θ to 180°. A least square computer program was prepared for this purpose.

In Fig. 2, the lattice parameters of CeSi$_x$ at room temperature are plotted. Our values agree quite satisfactorily with those on a large number of samples with different values of x reported by Lee *et al.* [2]. They claimed that the sample of CeSi$_{2.00}$ consists of two phases metallographically, and excluded this sample from their consideration. However, our X-ray powder diagram of the sample had neither extra impurity peaks, nor a broadening of diffraction peaks. Therefore, we have no reason to exclude this sample from our discussion.

With the decrease of x from 2.00 to 1.80, the value of c was observed to decrease linearly, while the value of a not to change appreciably. An orthorhombic GdSi$_2$ structure replaces the tetragonal–ThSi$_2$ structure for CeSi$_{1.70}$. The values of a and b for this sample are also shown in Fig. 2. The behaviour of these lattice parameters at 273 K is quite normal.

On the other hand, values of c at 10 K, also plotted in Fig. 2, are very complicated and peculiar. For CeSi$_{2.00}$, the value of c at 10 K is larger than that at 273 K. In contrast, for CeSi$_{1.85}$ and CeSi$_{1.70}$, the values

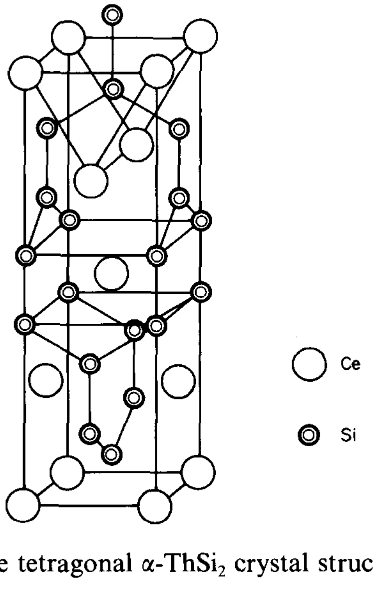

Fig. 1. The tetragonal α-ThSi$_2$ crystal structure.

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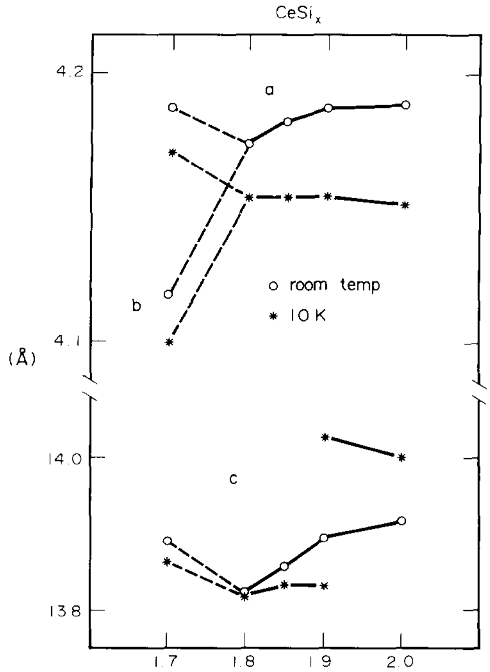

Fig. 2. Lattice parameters of CeSi$_x$ at 273 and 10 K.

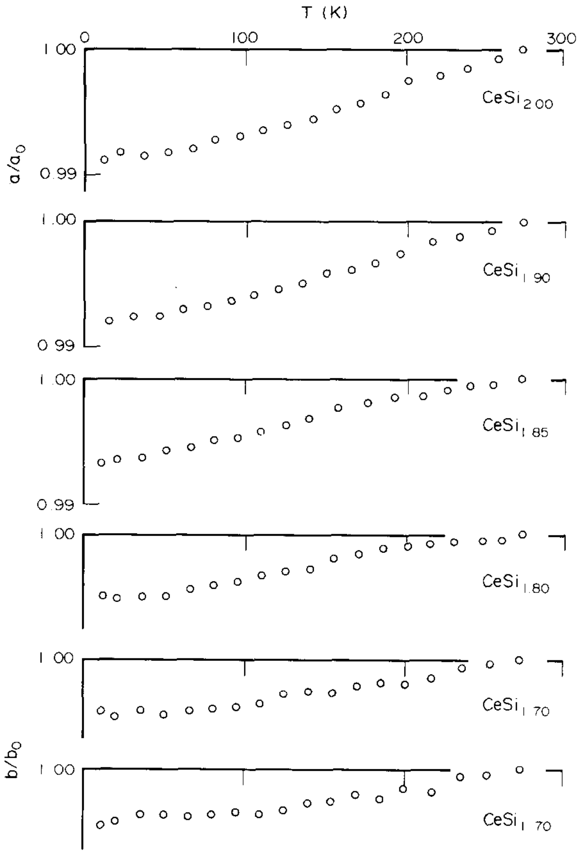

Fig. 3. Lattice parameters, a and b, divided by a_0 and b_0 at 273 K, respectively, are shown as a function of temperature for five samples of CeSi$_x$.

of c at 10 K are only slightly smaller than those at 273 K. Furthermore, the X-ray diffraction diagram of CeSi$_{1.90}$ was found to manifest a splitting of $(00l)$ peaks indicating a coexistence of two phases having different values of c, which we call hereafter the HT and LT phases, respectively. At 10 K, the value of c of the HT phase is larger than that at 273 K, while the value of c of the LT phase being smaller than that at 273 K. The mixing ratio of the HT phase to the LT phase is about 2 to 1 at 10 K on the ground of X-ray intensities of the two phases. However, we observed no splitting of $(ll0)$ peaks of this sample in a resolution of our experiment. Thus, the two phases have very nearly same values of a.

On the other hand, values of a and b at 10 K for all samples are smaller than those at 273 K. The difference of the lattice parameters at the two temperatures is in the order of a normal thermal expansion.

In order to investigate the complicated behaviour of lattice parameter c, diffraction measurements were repeated by changing the temperature from 10 to 273 K by a step of 10 to 15 K. The observed values of lattice parameters at various temperatures divided by those at 273 K, a/a_0, b/b_0 and c/c_0, are shown as the function of temperature in Figs. 3 and 4.

For CeSi$_{2.00}$, c was found to show an abnormal thermal contraction in a temperature range from 120 to 190 K, the total contraction being about 0.5%. Below and above this temperature range, c is almost constant. On the other hand, CeSi$_{1.90}$ consists of the HT and LT phases having different values of c at low temperature as mentioned before. As the increase of temperature, the X-ray peak intensities of the HT phase become stronger, while the peak intensities of the LT phase become weaker. The HT phase was found to show an abnormal thermal contraction in c from 150 to 200 K, while the LT phase show almost no change in c from 10 to 200 K.

CeSi$_{1.85}$ is found to have also the HT and LT phases similar to CeSi$_{1.90}$. However, the LT phase is dominating from 10 K to about 240 K. The HT phase starts to coexist at 250 K and this phase rapidly and completely replaces the second phase at 273 K. The HT phase disappears before showing the whole behaviour of the abnormal thermal contraction.

In comparison with CeSi$_{1.90}$ and CeSi$_{1.85}$, both of CeSi$_{1.80}$ and CeSi$_{1.70}$ samples show only a single phase behaviour. Values of c for these samples are nearly constant from 10 to 273 K. From their values of c, the observed phase is considered to be the LT phase, which predominates throughout the temperature

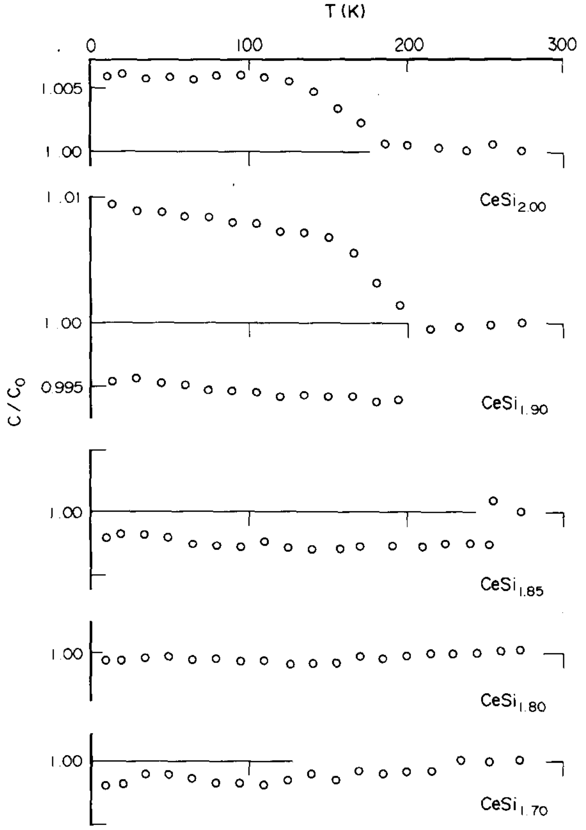

Fig. 4. Lattice parameter c divided y c_0 at 273 K is shown as a function of temperature for five samples of CeSi$_x$.

range of the observation. For both CeSi$_{1.80}$ and CeSi$_{1.70}$, if the HT phase should appear, it would be for a temperature higher than the room temperature.

On the other hand, a for all five samples and b for CeSi$_{1.70}$ were found to show a normal thermal expansion from 10 to 273 K. Diffraction peaks of ($ll0$) for CeSi$_{1.85}$ show no splitting similarly for CeSi$_{1.90}$. Therefore, the HT and LT phases of this sample also has nearly the same values of a.

Thus, the anomalies in thermal expansion and the occurrence of the phase transition in the present system are complicated and anisotropic, and depend delicately on the value of x of the samples.

The coexistence of ThSi$_2$ type crystal structure of different lattice parameters was found for CeSi$_{2-x}$Ga$_x$ system [5], which was discussed in connection with the Kondo-volume transition. However, for the samples in the present study, the magnetic susceptibility, a quantity directly related to the Ce ($4f$) electron state, does not show any anomaly [2], and the thermopower, a quantity known to be very sensitive to a delicate change of Ce ($4f$) electron state, shows only a faint break if any at the transition [6]. Therefore, the anomalous behaviour on the thermal expansion and the phase transition for the present samples may not be related with the Ce ($4f$) electron problem. We note that a phase transition very similar to these for CeSi$_{1.90}$ and CeSi$_{1.85}$ was reported for PrSi$_{2.00}$ [3, 4]. This fact supports the irrelevance of the Ce electron state to the phase transition in the present study.

Instead, we present here a possibility that they are related with a crystal instability which is characteristic of the crystal structure of present samples. In the crystal structure of α-ThSi$_2$, Si atoms form a three-dimensional graphite structure, and every Si atom has three Si neighbours and six Ce neighbours making a prism-shape as illustrated on the top part of the unit cell in Fig. 1. However, the distance from the Si atom in consideration (marked by a double circle) to the Si atom on its top is seen not to be exactly the same to the distance to the other two Si atoms, and the distance from the Si atom to the four Ce atoms on the top plane of the unit cell again not to be exactly the same to the other two Ce atoms. Therefore, the atomic potential of the crystal is expected to be asymmetric with a shallow minimum or even with a structure in the c crystal direction, while it is to be symmetric and with a deep minimum in the a direction.

When the temperature is high, the gain of entropy term may favour all Si–Si neighbours to be at the same distance. To account for the abnormal thermal contraction observed for CeSi$_{2.00}$, we tentatively sketch its free energy curve as the function of c in Fig. 5a and 5b. Its minimum is at $c = c_0$ at the room temperature (Fig. 5a). When the temperature becomes low, the minimum of the free energy may shift directly to the position of the minimum of the potential energy (Fig. 5b).

For CeSi$_{1.90}$ for CeSi$_{1.85}$, a new and second mini-

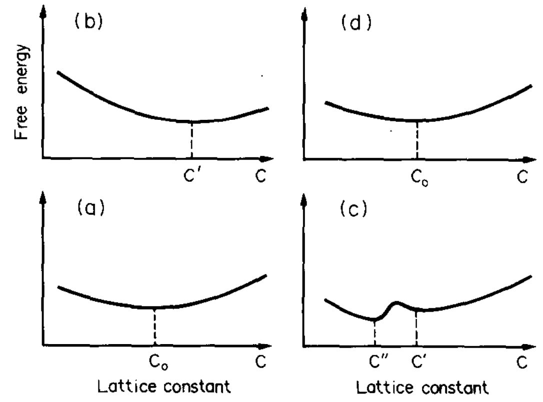

Fig. 5. Schematic free energy curves as the function of lattice parameter c for CeSi$_{2.00}$, (a) at the room temperature, (b) at low temperature, for CeSi$_{1.90}$ and CeSi$_{1.85}$, (c) at low temperature and (d) at the room temperature.

mum of the potential energy due to vacancies in the crystal sites may develop at low temperature at c'' smaller than c'. An existence of a potential barrier between these minima at c'' and c' (Fig. 5c) may explain the occurrence of the first order transition and the coexistence of the two phases for these samples. At high temperature, the gain of entropy term again may reduce the minimum of free energy back to c' as shown in Fig. 5d.

On the other hand, no abnormal thermal behaviours take place in the a direction, since the crystal potential energy is with a deep minimum in this direction.

It would be necessary to observe the internal parameter of Si position as the function of temperature in order to clarify the mechanism of anomalous behaviours of the present samples by an accurate intensity measurements of X-ray or neutron diffraction. The development of structure in the free energy due to vacancies in the crystal sites may be conjectured from the distortion from a tetragohnal α-ThSi_2 structure into an orthorhombic GdSi_2 structure for $\mathrm{CeSi}_{1.70}$.

Although our discussions presented above for the crystal instability is highly speculative, the resultant free energy curves shown in Fig. 5 are expected to be valid to explain the experimental data in Figs. 2–4.

Recently, so-called precursor phenomena at martensitic phase transition, in Fe–Pd alloys for example, have been reported [7]. Although this effect is quite different from the phase transition of CeSi_x in the present study, both try to consider the actual and complicated mechanism how the first order phase transition takes place in these samples.

A neutron diffraction study of the same samples by Kohgi *et al.* is noted to appear soon [8].

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