# Origin of multiple magnetic transitions in $CeSi_x$ systems

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(Received 21 April 1998; revised manuscript received 16 March 1999)

In this study, $CeSi_x$ alloys with Si compositions $x$ between 1.70 and 1.84 are shown to exhibit multiple steplike features or peaks in the ac susceptibility data in the 10–15 K temperature range which may be associated with different magnetic ordering temperatures. Depending upon annealing conditions, it is possible to obtain a single peak or two peaks for all compositions studied in the magnetic regime of the $CeSi_x$ system ($x<1.85$). The existence of multiple peaks is an intrinsic feature that is related to the Si vacancy distribution and is not necessarily a result of phase segregation. Our data also shed light on the inconsistency of various studies regarding the presence and absence of a spontaneous jump in magnetization versus magnetic field measurements at $T<T_c$. [S0163-1829(99)07833-9]

## INTRODUCTION

The $CeSi_x$ system ($1.55<x<2.0$) has been the object of numerous studies in the context of intermediate-valency, Kondo-lattice, and heavy-fermion phenomena in recent years.[1–16] Careful experiments[13] have shown that samples are always Si deficient and a stoichometeric $CeSi_2$ may not exist. Therefore, we will refer nominally to $CeSi_2$ as ''$CeSi_2$.'' The early investigations focused on the nonmagnetic ground state of ''$CeSi_2$.'' However, it is the broad homogeneity range of $CeSi_x$ ($1.55<x<2.0$) which attracted the greater attention, as it allows the variation of the magnetic strength of the Ce ions by varying the Si composition and provides an ideal environment for testing the so-called Kondo-lattice models.[17,18] Large values of the linear specific heat coefficient have been reported in this system,[6,13] which add another dimension of interest for the study of this system in the context of heavy-fermion phenomena.

The existence of $CeSi_2$ was reported as early as 1865,[19] and the Si-deficient phase was reported in 1968.[20] However, ground-state properties of this alloy system were first explored in the last decade.[2,3] The ''$CeSi_2$'' has a $ThSi_2$-type tetragonal structure,[21] and its ground state is nonmagnetic. A structural transformation occurs with increasing Si deficiency to the $GdSi_2$-type orthorhombic structure. This structural transformation occurs in $CeSi_x$ for Si compositions $x<1.84$, and a magnetic ground state emerges for compositions $x\leqslant1.85$.[3,9,10] Among the interesting features is the diverging nature of the specific heat coefficient $\gamma$ in the same composition range where the magnetic-nonmagnetic boundary lies.[6,13] Extensive investigations of this system have led to a considerable understanding of the physical properties, and a Kondo-lattice-like state has been established through electrical resistivity and magnetic susceptibility measurements in this system.[3,5,9,12] The Kondo-lattice-like behavior in this system has been further tested through the measurement of magnetic properties under high-pressure conditions.[10] The experimental results provide excellent

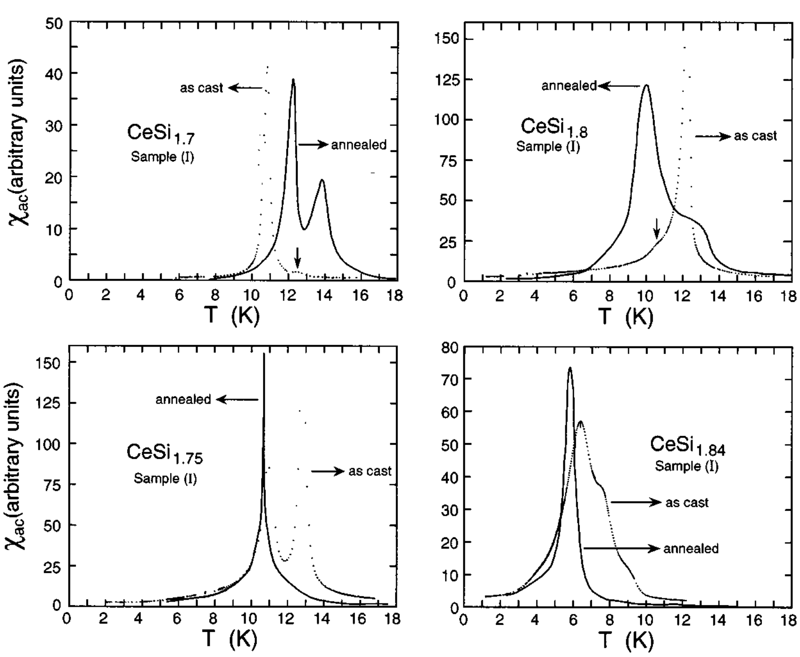


FIG. 1. The ac susceptibility data as a function of temperature for annealed and as-cast $CeSi_x$ samples (I).

 

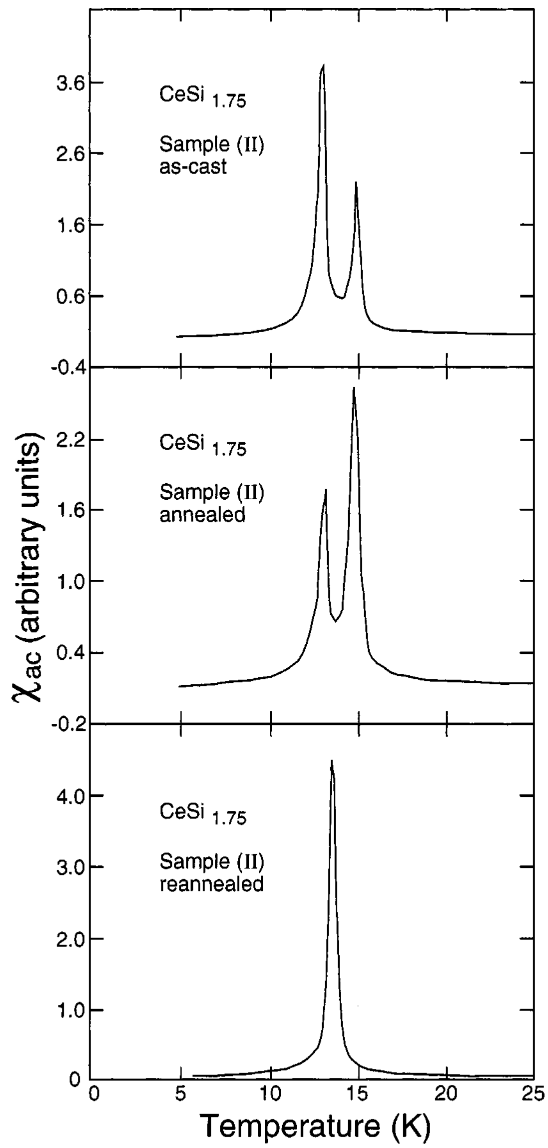


FIG. 2. The ac susceptibility data as a function of temperature for the as-cast, annealed, and reannealed $CeSi_{1.75}$ sample (II).

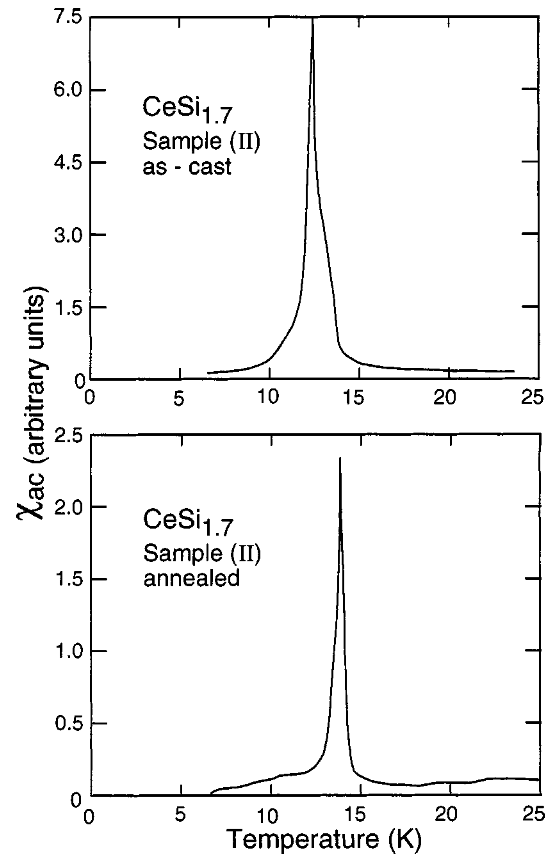


FIG. 3. The ac susceptibility data as a function of temperature for the as-cast and annealed $CeSi_{1.70}$ sample (II).

qualitative agreement with the theoretical predictions of the Kondo-lattice models.[10,11]

However, some features observed in this system have not yet been fully understood. For example, anomalies have been observed in the electrical resistivity versus temperature data in the vicinity of 250 K.[12,16,22] Also based on the electrical resistivity data, a Mott transition has been proposed in these alloys,[16] which needs to be confirmed. Lately, the existence of two tetragonal phases with slightly different lattice parameters (a low-temperature phase and high-temperature phase) have been reported[23–26] for samples with $CeSi_{1.86}$ and $CeSi_{1.90}$, and two magnetic phase transitions have been observed in studies on $CeSi_{1.70}$ single crystals.[8,15] In this paper we will discuss the latter aspect.

## EXPERIMENT

The samples of nominal compositions were produced by melting the proportionate amount of the constituents in a high-purity Ar (99.995%) atmosphere. The first set of samples (Sample I series) were prepared in a water-cooled Cu crucible in an induction furnace using commercial Ce (99.9 at. %, Kurt Rasmus and Co.) and Si (99.999 at. %, Wacker Chemetronics) at an Ar pressure of 1.3 bar. The remaining samples were prepared using vacuum-remelted Ce lumps (99.9 at. %, REaction grade, Alpha products) and Si (99.999 at. %, Alpha products) in an arc furnace under a flowing Ar atmosphere. In both cases, the samples of mass ~1 g were turned over and remelted 4–6 times to ensure homogeneity. The weight losses were typically <0.1%. All compositions are nominal. Half of each sample was wrapped in a Ta foil sealed in a quartz tube under high vacuum ($10^{-5}$–$10^{-6}$ Torr) and annealed at 1250–1273 K for 3 days. In some cases, the samples were reannealed for up to 8 days in the 1250–1273 K temperature range. Those samples are labeled ''reannealed'' in the text. The crystal structures of these alloys were determined by x-ray diffraction with Cu $K\alpha$ radiations using a Siemens D500 diffractometer.

ac magnetic susceptibility measurements were performed at 83–87 Hz using in-house-constructed probes, and no external field was applied during the measurements. A Quantum Design superconducting quantum interference device (SQUID) magnetometer was used for magnetization measurements.

Metallographic studies were performed on the first set of samples. The polished surfaces of the samples were examined under a microscope using monochromatic Na light. No traces of any secondary phase, big grains, and clean grain boundaries were typical features of the samples, except that the presence of a secondary phase was detected at the grain

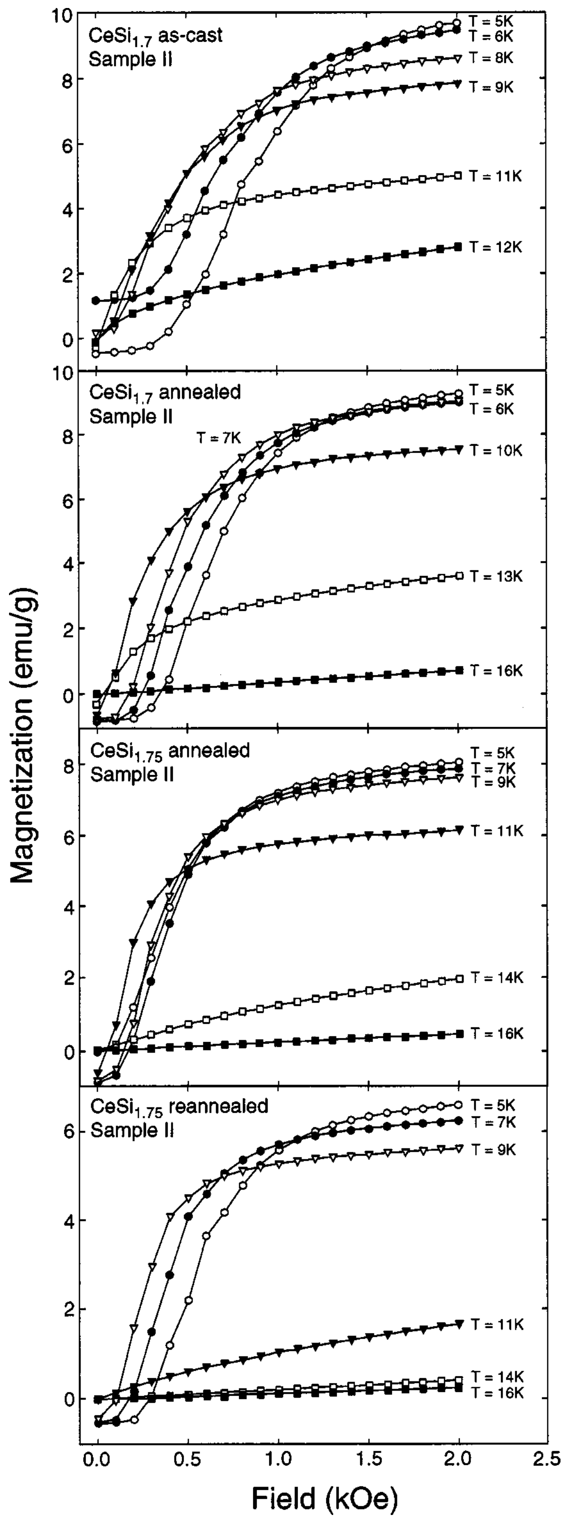


FIG. 4. The magnetization vs field data at various temperatures in fields up to 2 kOe for $CeSi_x$ samples (II).

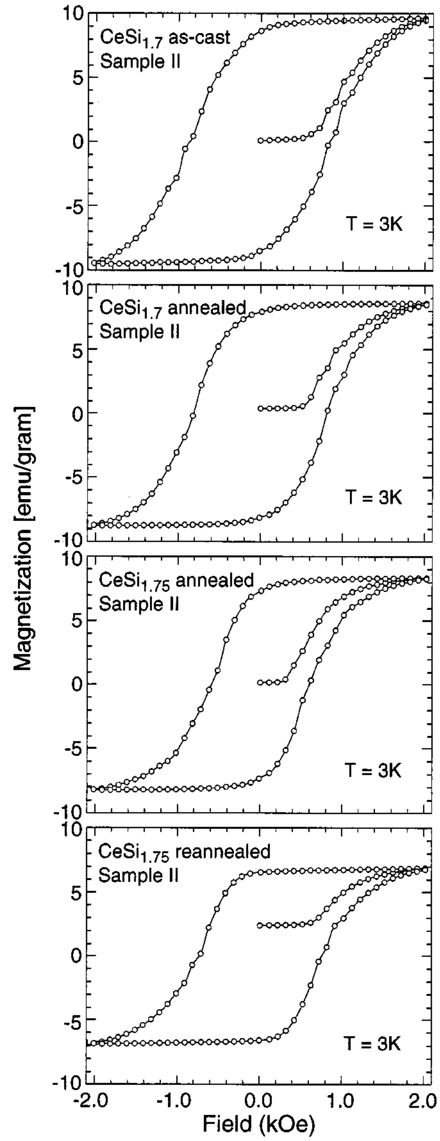


FIG. 5. The hysteresis loop measurement for $CeSi_x$ samples (II).

boundaries in the composition regime $x<1.7$ that is identified as the CeSi (1:1) phase by x-ray measurements. Scanning electron microscopy (SEM) studies were performed using Joel microscope and energy dispersive analysis on the second set of samples labeled as Sample 2 in the figures. No traces of a either a secondary phase or a compositional inhomogeneity were apparent. The samples are stable in the ambient atmosphere, and no degradation in physical appearance (color, shape) or structural and magnetic properties was noticed in the first set of samples that were exposed to the ambient environment for more than a decade. The structural and magnetic properties of samples prepared from different source of starting materials and different techniques are remarkably similar and do not show any marked difference based on preparation method or on different sources of starting materials.

## RESULTS AND DISCUSSION

Figure 1 shows the ac susceptibility measurements on the as-cast and annealed $CeSi_x$ samples. Noteworthy features are multiple steps in the data, which may be associated with multiple magnetic transition temperatures. The ac susceptibility data for the as-cast $CeSi_{1.75}$ sample (I) and as-cast $CeSi_{1.84}$ sample (I) exhibit multiple steplike features or peaks in the as-cast state, but only a single peak is observed for the above compositions in the annealed state. On the other hand, for both the as-cast $CeSi_{1.70}$ sample (I) and as-cast $CeSi_{1.80}$ sample (I) a single peak is apparent in the ac susceptibility

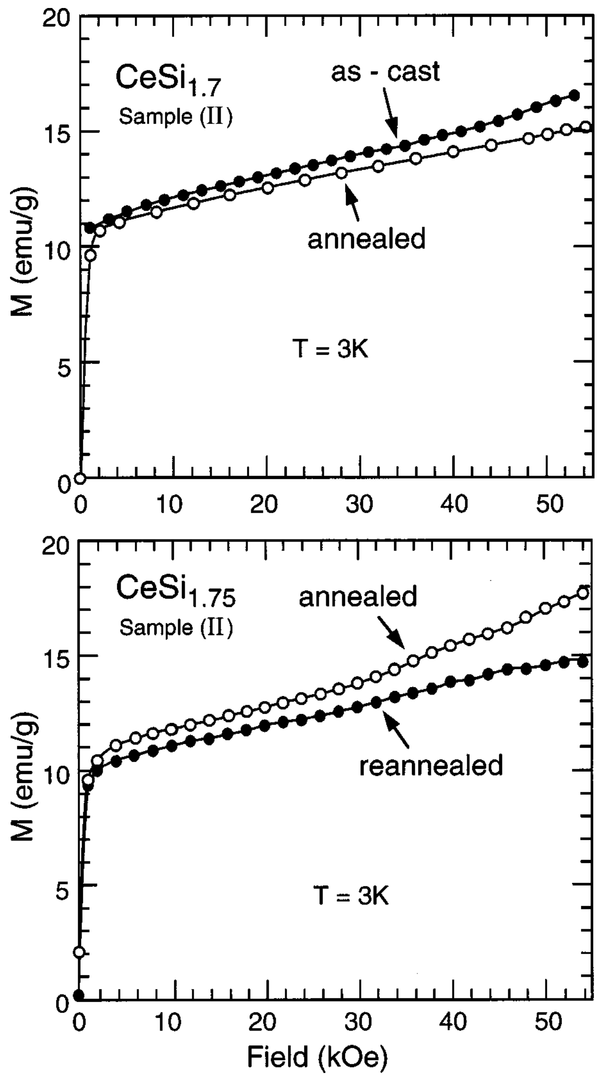


FIG. 6. The magnetization vs field data at 3.0 K in fields up to 50 kOe for $CeSi_x$ samples (II).

data and signatures of a possibly second minor peak are also present, which are indicated by arrows in Fig. 1. The annealed samples for the latter compositions have clearly two distinct peaks, which may be associated with the two magnetic ordering temperatures. There may be several reasons for observing multiple magnetic transitions in this system. One obvious factor that may be taken into consideration is the large homogeneity range of the $CeSi_x$ alloys. Due to the large homogeneity range, local composition variations may exist which may explain the observed behavior. It would also be consistent with the observation of two tetragonal phases for the $CeSi_{1.84}$ sample. Moreover, the origin of two peaks in $CeSi_{1.70}$ has been ascribed to two different types of magnetic order (antiferromagnetic and ferromagnetic) in a neutron diffraction study. In order to test the occurrence of multiple magnetic transitions and to understand their origin, we made investigations on additional samples. In these studies we focused on the $CeSi_{1.70}$ and $CeSi_{1.75}$ compositions.

Figure 2 shows the ac susceptibility data on a $CeSi_{1.75}$ sample (II) which was measured in the as-cast, annealed (1250 K, 3 days), and reannealed state (1250 K, 8 days; i.e., the total annealing time is $3+8=11$ days). The two-peak structure which was apparent in the as-cast state in sample (I) is also apparent in the as-cast state in this sample (sample II). The intensity ratio of the two peaks changes on annealing, and finally they merge into a single peak on reannealing. The ac susceptibility measurements on another $CeSi_{1.75}$ sample (III) showed a single-peak structure in both as-cast and annealed states (not shown here). It may be pointed out that preparatory conditions were identical for samples II and III.

The ac susceptibility data on a $CeSi_{1.70}$ sample (II) are displayed in Fig. 3. The ac susceptibility data exhibit an unsymmetrical single peak in the as-cast state indicating the presence of a smaller peak at the high-temperature side of the main peak. The two peaks merge into a single peak on annealing, and peak position shifts towards the higher temperature. A third $CeSi_{1.70}$ sample (III) produced results identical to the $CeSi_{1.70}$ sample (I), which are not shown here. Thus samples prepared under identical conditions may exhibit a single or multiple magnetic transitions depending on annealing conditions for any composition in the magnetic regime. However, when sufficient annealing time is provided, each sample can be shown to exhibit a single peak in the ac susceptibility, but the annealing time for obtaining such a state varies from sample to sample. The tendency for this type of behavior is probably related to the mobility and distribution of vacancies in the samples. It is logical to assume that each heat treatment results in a different statistical distribution of vacancies. That is why similar heat treatments (same temperature, same duration) on different compositions or on two pieces of the same sample and even multiple treatments of the same sample piece may not reveal identical results.

To test the possibility of associating two peaks to two different types of magnetic orders, namely antiferromagnetic and ferromagnetic orders, low-field magnetization measurements were performed on both $CeSi_{1.70}$ and $CeSi_{1.75}$ samples. The measurements of magnetization versus applied field data at various temperatures are displayed in Fig. 4. In these measurements, the samples were brought to a temperature above the magnetic ordering temperature and were then cooled below the ordering temperature in zero applied field to obtain the so-called virgin state. However, depending on the trapped flux in the superconducting magnet of the SQUID magnetometer, the samples had a net positive or negative magnetization in a nominal zero external field. The magnetization initially showed a slow response to the external field and above a certain field value rose sharply and then showed a trend towards saturation. Such a behavior could possibly be associated with flipping of the antiferromagnetic spins. The trend is similar in both samples, and the sharply rising region shifts towards lower field values as the temperature increases. There is no marked difference in the curves in the temperature range where the two peaks are observed in the ac susceptibility data. However, if the samples had an antiferromagnetic component, then the sharp rise associated with the flipping of spins will also be followed by a sharp drop in the same field range when the field is reduced. However, no such drop is observed; rather the samples show the high remanence and coercivity of a ferromagnetic material, as can be seen in the hysteresis loop measurements shown in Fig. 5.

Another puzzle has been the observation of a jump in the magnetization along the nonaxial direction of $CeSi_{1.70}$ single crystals in the magnetization versus field data at low temperature in one measurement[15] and its absence in another measurement.[27] This jumplike feature, which occurs at about $H=30-35$ kOe, was also observed in the polycrystalline data in a previous study.[10] In Fig. 6 is shown the magnetization versus field data on the $CeSi_{1.70}$ sample (II) and $CeSi_{1.75}$ sample (II) that shed light on this aspect. After the initial sharp rise in the small fields, the magnetization continues to increase slowly at all fields at all temperatures, with a small positive slope. However, as the temperature is lowered, the magnetization starts increasing at a faster rate as the field values exceed the 30–35 kOe range, indicating a sudden increase in magnetization in this field range. In order to find the correlation between the presence of the peaks in the ac susceptibility with the jump in the magnetization in the 30–35 kOe range, a comparison of the data taken at 3.0 K is made in Fig. 6. An upward rise in the magnetization is apparent at about $H=30$ kOe in the data on the as-cast $CeSi_{1.70}$ sample (II) and annealed $CeSi_{1.75}$ sample (II) which exhibited two magnetic ordering peaks in the ac susceptibility measurements (Figs. 2 and 3). In contrast, no such anomaly is apparent in the magnetization versus field data on the annealed $CeSi_{1.70}$ sample (II) and reannealed $CeSi_{1.75}$ sample (II), which showed a single magnetic ordering peak in the ac susceptibility data (see Figs. 2 and 3). Sato *et al.*[8,15] suggested that these jumps in the magnetization versus field data at about 35 kOe are associated with an antiferromagnetic modulation along the *c* axis below the ferromagnetic ordering temperature. Our data suggest that these jumps are also dependent on the presence of the multiple peaks in the ac susceptibility data and can be reduced in size and/or completely destroyed by proper heat treatments. Our results may provide a logical understanding for the presence of magnetization jumps in some studies[10,8,15] and also for the absence of magnetization jumps in other studies.[27]

In summary, we have shown that, depending on annealing conditions, either a single peak or multiple peaks associated with the magnetic ordering of Ce are observed in the $CeSi_x$ series for $1.7<x<1.84$. This behavior is attributed to the mobility and distribution of Si vacancies in the lattice. In our view, all observations point towards the stability of a simple ferromagnetic ground state in the $CeSi_x$ series with $1.67\leqslant x\leqslant 1.85$ if a statistically uniform distribution of Si vacancies is achieved in the lattice. However, a uniform Si vacancy distribution is generally not observed and complexities in structural and magnetic behavior arise. The observations of two tetragonal phases with slightly different lattice parameters, multiple ordering temperatures, and the presence of antiferromagnetic coupling layers are all related to the nonuniform distribution of Si vacancies in the lattice in a complex manner.


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