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Gamma to Alpha

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# for Philosophical Mag. Letters

## Neutron diffraction study on $\gamma \leftrightarrow \alpha$ phase transition in $\text{Ce}_{0.9}\text{Th}_{0.1}$ alloy

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Comprehensive neutron diffraction measurements were performed to study the isostructural  $\gamma \leftrightarrow \alpha$  phase transition in  $\text{Ce}_{0.9}\text{Th}_{0.1}$  alloy. Using Rietveld refinements, we obtained lattice and thermal parameters as a function of temperature. From the temperature slope of the thermal parameters, we determined Debye temperatures  $\Theta_D^\gamma = 133(1)$  K and  $\Theta_D^\alpha = 140(1)$  K for the  $\gamma$  phase and the  $\alpha$  phase, respectively. This result implies that the vibrational entropy change is not significant at the  $\gamma \leftrightarrow \alpha$  transition, contrary to that from elemental Cerium [Phys. Rev. Lett. 92, 105702, 2004].

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### INTRODUCTION

Cerium metal is an intriguing material which displays rich phases as a function of temperature and pressure. At ambient pressure, elemental Ce undergoes a series of phase transitions from bcc to fcc to dhcp (double hexagonal close-packed) then back to fcc structures as the temperature decreases from its melting temperature ( $T_m \sim 1100$  K) to 100 K [1]. Among these multiple phase transitions, the isostructural (fcc)  $\gamma \rightarrow \alpha$  transition has been a long-standing research topic [2-7] since its first discovery by Bridgman in the 1930's [8]. The  $\gamma \rightarrow \alpha$  phase transition occurs at room temperature for pressures  $\sim 0.8$  GPa, as well as at ambient pressure and temperature  $\sim 100$  K, with a volume collapse of  $\sim 17\%$  [1].

This anomalously large volume change at the  $\gamma \rightarrow \alpha$  transition is commonly described by an instability of the single  $4f^1$  electron in either Mott transition [9] or Kondo-volume-collapse models [3]. In the Mott model, the delocalization of the  $4f$  electron in the  $\alpha$  phase provides the energy for the transition. In contrast, the Kondo spin fluctuations provide the driving force for the transition in the Kondo-volume-collapse model. In these models, however, lattice vibrational entropy and electron-lattice coupling are not considered, despite the large volume collapse which accompanies the valence change at the transition.

Regarding the vibrational entropy change at the  $\gamma \rightarrow \alpha$  phase transition, contradictory results exist. According to measurements on the  $\text{Ce}_{0.9}\text{Th}_{0.1}$  alloy by Lawson *et al.*, the Debye temperature for the  $\gamma$  and the  $\alpha$  phases are  $\Theta_D^\gamma = 145$  K and  $\Theta_D^\alpha = 142$  K, respectively [10]. This result implies that there is virtually no vibrational entropy change between the  $\gamma$  and the  $\alpha$  phases. Similarly, Manley *et al.* found in  $\text{Ce}_{0.9}\text{Th}_{0.1}$  that the phonon density of

states shows little change between the  $\gamma$  phase at 150 K and the  $\alpha$  phase at 140 K [11]. By contrast, Jeong *et al.* reported from neutron diffraction measurements on elemental Cerium that the vibrational entropy change is almost half of total entropy change at the  $\gamma \rightarrow \alpha$  transition [5], and, thus, claimed that vibrational entropy plays an important role in stabilizing the  $\gamma$  phase of elemental Ce.

To attempt to resolve the discrepancies between previous measurements of the vibrational entropy change at the  $\gamma \leftrightarrow \alpha$  transition in  $\text{Ce}_{0.9}\text{Th}_{0.1}$  and pure Ce, we have undertaken a new set of elastic neutron diffraction measurements to determine the vibrational properties of  $\text{Ce}_{0.9}\text{Th}_{0.1}$ . Our new measurements have the advantage of a higher neutron flux and detection efficiency than was available in previous measurements [10].

### EXPERIMENTS

At ambient pressure elemental Ce undergoes a  $\gamma \rightarrow \beta$  phase transition before it enters the  $\alpha$  phase with decreasing temperature. The formation of  $\beta$ -Ce phase is complicated, depending on the cooling history, and it is difficult to remove  $\beta$  phase once it is formed [1]. One way to avoid the formation of the  $\beta$ -Ce and to induce a direct  $\gamma \rightarrow \alpha$  phase transition, is by making an alloy, for example, with Th [12]. We prepared a  $\text{Ce}_{0.9}\text{Th}_{0.1}$  alloy arc melting of 99.99% metals in an atmosphere of Ar. The ingot was melted several times and then annealed for 5 days at 480 °C [4]. To examine the transition temperature and a response of lattice during cooling, we measured the thermal expansion coefficient using a differential capacitive dilatometry [13] as shown in Fig. 1. Here we notice that the thermal expansion coefficient becomes anomalously large near the transition temperature,  $T \simeq 120$  K. In ad-

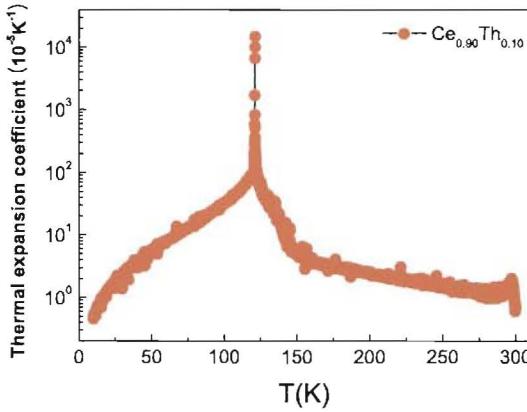


FIG. 1: Thermal expansion coefficient  $\alpha$  of  $\text{Ce}_{0.9}\text{Th}_{0.1}$  from 300 K to 10 K. The diverging behavior of  $\alpha$  indicates a discontinuous change of lattice parameter at the transition,  $T \approx 120$  K.

dition, the diverging behavior of  $\alpha$  at the transition indicates a discontinuous change of lattice parameter. These abnormal behaviors suggest deep involvement of the lattice in the phase transition.

For the time-of-flight neutron diffraction measurements, the sample was loaded in a vanadium can in a Helium environment to avoid oxidization, and then mounted in a closed-cycle helium dispex refrigerator. Neutron diffraction data were taken from 300 K  $\rightarrow$  20 K (cooling) and from 20 K  $\rightarrow$  250 K (warming) on the HIPD instrument at the Los Alamos Neutron Science Center.

## RESULTS AND DISCUSSION

Figure 2 shows diffraction patterns (back scattering bank at 153°) of the  $\gamma$  phase at 290 K and the  $\alpha$  phase at 20 K, with the corresponding Rietveld fits for a  $Fm\bar{3}m$  structure obtained using GSAS program [14]. Lattice, thermal, and peak profile parameters were refined, and absorption and background corrections were applied. During the cooling cycle, the  $\gamma$  phase does not disappear completely, even well below the transition temperature. Similarly, mixed  $\gamma$  and  $\alpha$  phases were found above the transition temperature during the warming cycle. Therefore, two-phase modeling was used for the Rietveld refinements near the transition temperature. Table 1 shows the relative volume fraction of the  $\alpha$  and  $\gamma$  phases during cooling.

Figure 3 shows the lattice parameter as a function of temperature. As the temperature decreases, the lattice parameter drops about 4.5% at around  $T \approx 117$  K, indicating the first-order nature of the transition. On the warming cycle, the transition occurs around  $T \approx 172$  K

TABLE I: Relative volume fraction of the  $\gamma$  and  $\alpha$  phases during cooling.

Temperature (K)	Relative fraction (%)	
	$\gamma$ -Ce	$\alpha$ -Ce
125	82	18
120	51	49
115	39	61
90	18	82
65	11	89
40	9	91
20	9	91

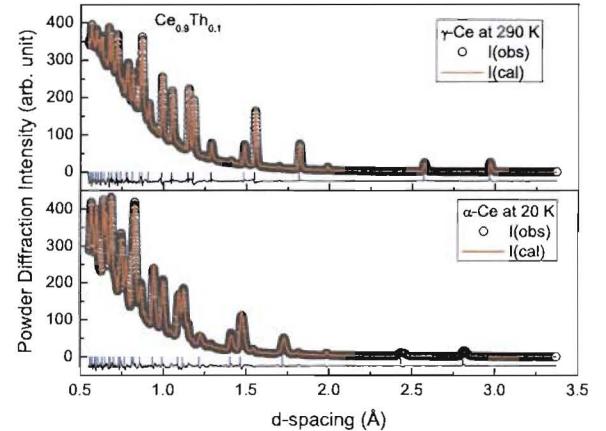


FIG. 2: Time-of-flight neutron powder diffraction patterns of  $\text{Ce}_{0.9}\text{Th}_{0.1}$  (a)  $\gamma$  phase at  $T=290$  K and (b)  $\alpha$  phase at  $T=20$  K with corresponding Rietveld fits (solid line). Tick marks indicate positions of the Bragg reflections. Also shown are difference curves.

with large temperature hysteresis. This behavior is quite similar to that observed in the  $\text{Ce}_{0.74}\text{Th}_{0.26}$  alloy, [15] except that the discontinuity is larger in  $\text{Ce}_{0.9}\text{Th}_{0.1}$ . Actually, the resistivity versus temperature measurement shows that the first-order step decreases with further addition of thorium, and disappears at the critical composition ( $x \approx 0.264$ ) [16]. In addition, recent studies on  $\text{Ce}_{0.9-x}\text{La}_x\text{Th}_{0.1}$  alloys [4] showed that the volume change between the  $\gamma$  and  $\alpha$  phases decreases exponentially with the doping of lanthanum ion, and the transition changes from being first-order to continuous at a critical concentration  $x_c \approx 0.14$ . These results indicate that the addition of thorium and lanthanum ions significantly influences the  $\gamma \rightarrow \alpha$  phase transition behavior of Ce-alloys.

We also note that the temperature dependence of the lattice parameter in the  $\gamma$  phase is not that of typical thermal contraction. In consistent with the thermal expansion behavior of the  $\gamma$ -phase, the lattice parameter shows downward curvature between 300 K and 120 K as shown in the inset of Fig. 2. For comparison, we plot the

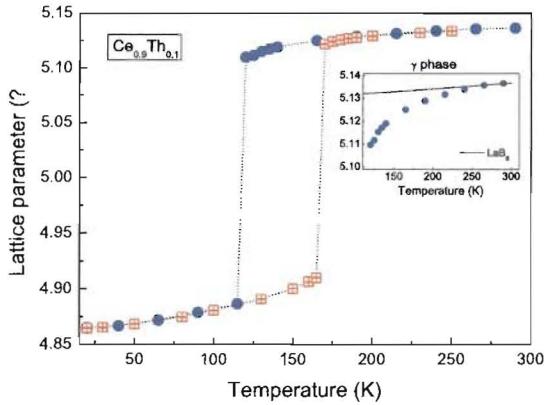


FIG. 3: Lattice parameter of  $\text{Ce}_{0.9}\text{Th}_{0.1}$  alloy as a function of temperature. The magnitude of error is comparable to the symbol size. The transition occurs around  $T \simeq 117$  K and  $T \simeq 172$  K during cooling and warming, respectively. The lattice parameter changes about 4.5% at the  $\gamma \rightarrow \alpha$  transition. The inset shows the lattice parameters of the  $\gamma$  phase (closed circle) and  $\text{LaB}_6$  (solid line) as a function of temperature.

lattice parameter of cubic  $\text{LaB}_6$  (solid line in the inset), which is rescaled to match that of the  $\text{Ce}_{0.9}\text{Th}_{0.1}$  alloy at 290 K. In this case, the lattice parameter exhibits linear temperature dependence with a thermal contraction less than 0.1% [17].

The anomalous temperature dependence of the lattice parameter in  $\text{Ce}_{0.9}\text{Th}_{0.1}$  alloy has been considered as an effect of valence fluctuation. Since the ionic radius of  $\text{Ce}(4f^1)^{+3}$  is about 9% greater than that of  $\text{Ce}(4f^0)^{+4}$  [18], a localization and delocalization behavior of the  $4f^1$  electron can cause a huge changes in the lattice parameter. Therefore, the lattice parameter has been used to estimate the valence of Ce and the fractional occupancy of the  $4f^1$  level. Following the approach of Shapiro *et al.* [15], we first calculated the lattice parameter of an equivalent Ce sample using the Vegard's law, that is,

$$a_{Ce} = \frac{1}{1-x} (a_{Ce_{1-x}\text{Th}_x} - x a_{\text{Th}}), \quad (1)$$

where  $a_{\text{Th}}=5.0741$  Å was used [19]. No correction for thermal expansion was applied because the thermal effect is negligible compared to the contraction due to the valence change, as we discussed earlier. Then, the fractional occupancy of  $4f^1$  level and average valence are interpolated using the lattice parameters of  $a(\text{Ce}^{3+})=5.221$  Å and  $a(\text{Ce}^{4+})=4.661$  Å [20]. Figure 4 shows the results. As the temperature decreases the valence of Ce increases gradually and jumps at the the transition temperature. With further decrease of temperature the valence increases gradually. Even though the approximation used in this estimation is crude, it is clear that the

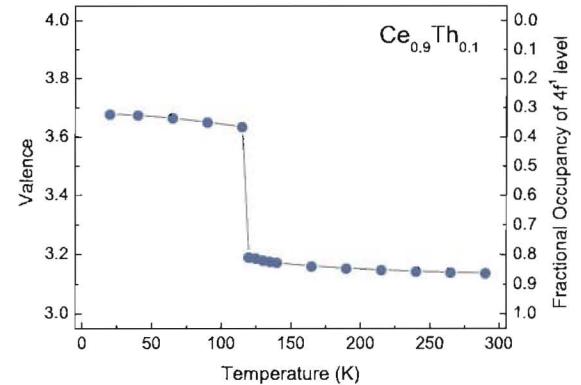


FIG. 4: Valence of Ce and the fractional occupancy of the  $4f^1$  level obtained from the lattice parameter of  $\text{Ce}_{0.9}\text{Th}_{0.1}$  as a function of temperature.

$4f$  ion is not either fully localized nor fully delocalized at all temperatures [7].

Now we discuss lattice vibrations in the  $\gamma$  and  $\alpha$  phases of  $\text{Ce}_{0.9}\text{Th}_{0.1}$ . Figure 5 shows the isotropic thermal displacements  $\langle u_{iso}^2 \rangle$  of Ce as a function of temperature. Closed circles represent measurements performed with decreasing temperature and open squares with increasing temperature. The magnitude of  $\langle u_{iso}^2 \rangle$  can be affected by background, absorption corrections, and uncertainties in the incident neutron spectra. Thus, the Debye temperatures are determined from the slopes of the thermal displacement as a function of temperature, assuming a temperature-independent offset, as in Eq. (2) below. The solid lines are fits using Eq. (2), with Debye temperatures  $\Theta_D^\gamma=133(1)$  K and  $\Theta_D^\alpha=140(1)$  K,

$$\langle u^2 \rangle_{\text{measured}} = \langle u^2 \rangle_{\text{offset}} + \frac{3\hbar}{M\omega_D} \left[ \frac{1}{4} + \left( \frac{T}{\Theta_D} \right)^2 \Phi_1 \right], \quad (2)$$

where  $\Phi_1 = \int_0^{\Theta_D/T} x(e^x - 1)^{-1} dx$ ,  $\Theta_D$  ( $=\hbar\omega_D/k_B$ ) is the Debye temperature, and  $\langle u^2 \rangle_{\text{offset}}$  is a temperature-independent offset.

Here we point out the Debye temperature change ( $\Theta_D^\gamma=133$  K  $\rightarrow$   $\Theta_D^\alpha=140$  K) in  $\text{Ce}_{0.9}\text{Th}_{0.1}$  is much smaller than the corresponding change ( $\Theta_D^\gamma=104$  K  $\rightarrow$   $\Theta_D^\alpha=133$  K) in elemental Ce. Thus, the vibrational entropy change,  $\Delta S_{\text{vib}}^{\gamma \rightarrow \alpha} \approx 3k_B \ln \left( \Theta_D^\alpha / \Theta_D^\gamma \right)$  [21], is not significant for the  $\text{Ce}_{0.9}\text{Th}_{0.1}$  alloy. Note that this result is consistent with the inelastic measurement on  $\text{Ce}_{0.9}\text{Th}_{0.1}$  by Manley *et al.*. Therefore, our result suggests that the discrepancy in the vibrational entropy change from diffraction measurements on elemental Ce and from inelastic measurements on  $\text{Ce}_{0.9}\text{Th}_{0.1}$  is not due to the difference in measurements methods. Instead, we suggest that the alloying of Ce by Th significantly affects the

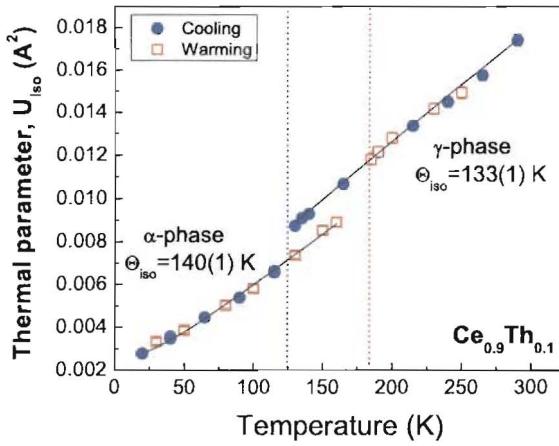


FIG. 5: Isotropic thermal displacements of  $\text{Ce}_{0.9}\text{Th}_{0.1}$  vs temperature during cooling (circle) and warming (square) cycles. The size of error bar is comparable to the size of symbols. Solid lines are fits to Eq. (2) with Debye temperatures  $\Theta_D^\gamma=133(1)$  K and  $\Theta_D^\alpha=140(1)$  K.

elastic properties of the Ce-Th alloy, as a few percent of Mg influences the Young's modulus of Ce-Mg alloy [22].

## SUMMARY

In summary, we performed neutron diffraction measurements on  $\text{Ce}_{0.9}\text{Th}_{0.1}$  alloy, and studied the temperature dependence of the lattice and thermal parameters across the  $\gamma \leftrightarrow \alpha$  phase transitions. For the  $\text{Ce}_{0.9}\text{Th}_{0.1}$  alloy the difference in Debye temperatures between the  $\gamma$ - and  $\alpha$ -phase is much smaller than the corresponding change in elemental Ce, consistent with the inelastic neutron scattering measurements on  $\text{Ce}_{0.9}\text{Th}_{0.1}$  alloy. This result implies that the addition of thorium ion to Ce significantly influences the elastic properties besides its phase transition behavior.

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