

Double $4f$ collapse in $\text{Ce}_{0.9-x}\text{Yb}_x\text{Th}_{0.1}$

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Simultaneous sharp changes in the energy of K x-ray lines of Ce and Yb have been observed experimentally in $\text{Ce}_{0.9-x}\text{Yb}_x\text{Th}_{0.1}$. These changes are reversible as the temperature is varied. The effect is shown to be due to a delocalization of $4f$ electrons of Ce and Yb (the electronic transitions Ce^{3+} , $4f^1\text{-Ce}^{4+}$, $4f^0$, Yb^{2+} , $4f^{14}\text{-Yb}^{3+}$, $4f^{13}$).

The effect of the external conditions (the pressure and the temperature) on the macroscopic and microscopic properties of Ce has been studied extensively. The research interest stems primarily from the unique features of the first-order isomorphic phase transition $\text{Ce}_\gamma\text{-Ce}_\alpha$ and the phenomenon of mixed valence (or "intermediate valence" or "valence fluctuation"), which has been the subject of active research in recent years (Ref. 1, example). The characteristics of the $\text{Ce}_\gamma\text{-Ce}_\alpha$ transition (the temperature, the pressure, the type of transition, the coordinates of the critical point, the volume effect, etc.) which are important for reaching an understanding of the physics of mixed valence can be varied by inserting impurities of other elements in the Ce lattice. The microscopic properties of Ce in these materials (the filling of the $4f$ shell, the degree of removal of the $4f$ electron from the atom in the course of the transition, etc.), however, have not been studied adequately. To the best of our knowledge, there are no direct experimental data on the electronic structure (or on its changes) of an impurity atom incorporated in the lattice.

Among all of the rare-earth elements, those which have the greatest effects on the $\text{Ce}_\gamma\text{-Ce}_\alpha$ transition are Eu and Yb (Refs. 2 and 3). The "poisoning" of Ce by small amounts (a few percent) of Eu or Yb sharply reduces the volume effect; the transition temperature decreases anomalously rapidly with increasing impurity concentration; etc.

In this letter we report a study of the electronic state (the filling of the $4f$ shell) of Ce and Yb in $\text{Ce}_{0.9-x}\text{Yb}_x\text{Th}_{0.1}$ ($0 \leq x \leq 0.2$) at temperatures above ($T = 300$ K) and below ($T = 77$ K) the temperature of the $\text{Ce}_\gamma\text{-Ce}_\alpha$ transition ($T_{tr} = 160$ K). Our study was based on the shifts of x-ray lines.⁴ (The addition of 10% Th to the Ce–Yb system prevents the formation of $\beta\text{-Ce}$ at a low temperature.⁴)

The single-phase solid solutions of $\text{Ce}_{0.9-x}\text{Yb}_x\text{Th}_{0.1}$ synthesized by arc melting had an fcc structure. The lattice constant increased essentially linearly with increasing x in the composition range studied (see the inset at the top of Fig. 1).

In the experiments we measured the energy difference (or shift) ΔE of the $K\beta_1$ line of Ce and the $K\alpha_1$ line of Yb of a test sample, held at $T = 300$ or 77 K with respect to a reference sample (metallic Ce or Yb). The difference between the number of $4f$

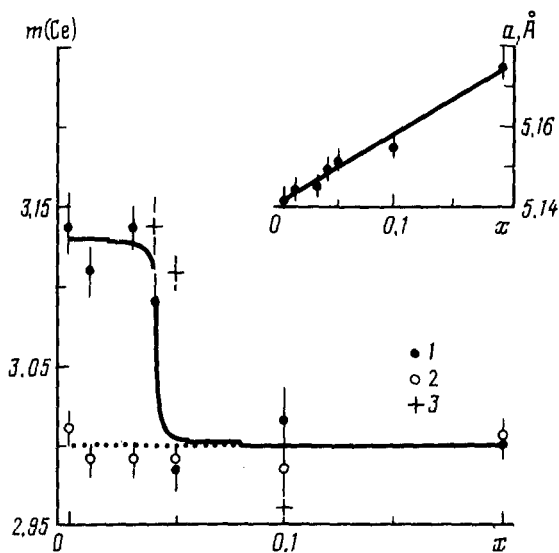


FIG. 1. The valence of Ce, $m(\text{Ce})$, in $\text{Ce}_{0.9-x}\text{Yb}_x\text{Th}_{0.1}$ versus the composition. 1— $T = 77$ K; 2— $T = 300$ K; 3— $T = 77$ K, after the sample has been cooled to $T = 4.2$ K. The inset at the top shows the lattice constant of $\text{Ce}_{0.9-x}\text{Yb}_x\text{Th}_{0.1}$ versus x .

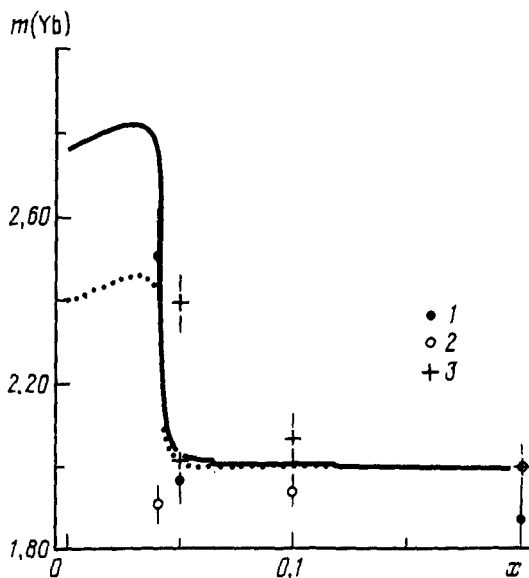


FIG. 2. The valence of Yb, $m(\text{Yb})$, in $\text{Ce}_{0.9-x}\text{Yb}_x\text{Th}_{0.1}$ versus the composition. 1— $T = 77$ K; 2— $T = 300$ K; 3— $T = 77$ K, after the sample has been cooled to $T = 4.2$ K. The solid and dotted lines show numerical calculations for (solid line) $n_{\text{cr}}(\text{Ce}) = n_{\text{cr}}(\text{Yb}) = 1$ and dotted line) $n_{\text{cr}}(\text{Ce}) = 2$, $n_{\text{cr}}(\text{Yb}) = 1$.

electrons per Ce ion or Yb ion (the valence) in the test sample and in the reference was determined by the method of Ref. 5.

Figures 1 and 2 show the experimental valences of Ce and Yb in the alloys studied versus the composition at $T = 300$ and 77 K. It can be seen from Fig. 1 that a cooling of the $\text{Ce}_{0.9-x}\text{Yb}_x\text{Th}_{0.1}$ samples from the region $x \lesssim 0.05$ induces an electronic transition from a trivalent state of Ce (open circles) to a mixed-valence state (filled circles), similar to the $\text{Ce}_\gamma\text{-Ce}_\alpha$ transition in pure Ce (Ref. 4, for example). The poisoning of Ce by small admixtures of Yb results in a suppression of the $\text{Ce}_\gamma\text{-Ce}_\alpha$ transition: The Ce valence falls from $\bar{m}_{\text{Ce}}(x = 0 - 0.04) = 3.12 \pm 0.01$ to $\bar{m}_{\text{Ce}}(x \gtrsim 0.05) = 3.00 \pm 0.01$.

Accompanying the $4f$ collapse in the Ce atom at a low temperature we observe a $4f$ collapse in the Yb atom (Fig. 2): The valence of Yb decreases sharply at $x \approx 0.05$ from $m_{\text{Yb}} = 2.42 \pm 0.05$ to $\bar{m}_{\text{Yb}}(x \gtrsim 0.05) = 1.99 \pm 0.02$ (these simultaneous changes in the valence of Ce and Yb in $\text{Ce}_{0.9-x}\text{Yb}_x\text{Th}_{0.1}$ are reversible as the temperature is varied).

The valence of Ce and Yb in the alloy in the vicinity of the critical concentration ($x_{\text{cr}} \approx 0.05$) also depends on the history of the sample. For a $\text{Ce}_{0.85}\text{Yb}_{0.05}\text{Th}_{0.1}$ sample cooled to $T = 4.2$ and heated to $T = 77$ K, for example, we find $m_{\text{Ce}}(77 \text{ K}) = 3.11 \pm 0.01$ and $m_{\text{Yb}}(77 \text{ K}) = 2.39 \pm 0.05$, while for the same sample cooled from $T = 300$ K to $T = 77$ K we find $m'_{\text{Ce}}(77 \text{ K}) = 2.98 \pm 0.02$ and $m'_{\text{Yb}}(77 \text{ K}) = 1.98 \pm 0.05$ (the plus signs and filled circles in Figs. 1 and 2.¹⁾

Shaburov *et al.*⁵ have shown that Ce in mixed-valence compounds has a valence of ≈ 3.13 , ≈ 3.27 , or ≈ 3.39 . This effect is explained on the basis that different final states of the $4f$ electron in the transition to the mixed-valence state correspond to different valences. Working on the basis of Ref. 5, we can represent the electronic structure of Ce in $\text{Ce}_{0.9-x}\text{Yb}_x\text{Th}_{0.1}$ in the mixed-valence phase ($T = 77$ K, $x \lesssim 0.05$) as a resonance (as fluctuations) among the Ce^{3+} , $4f^7\text{-Ce}^{4+}$, $4f^0$ states: The experimental valence $\bar{m}_{\text{Ce}}(x = 0 - 0.04, T = 77 \text{ K}) = 3.12 \pm 0.01$ agrees well with the valence calculated for this version, $m_{\text{calc}} = 3.14$.

The suppression of the $\text{Ce}_\gamma\text{-Ce}_\alpha$ transition in $\text{Ce}_{0.9-x}\text{Yb}_x\text{Th}_{0.1}$ by ytterbium can be understood qualitatively on the basis of the following arguments: The mixed-valence state is achieved under the condition $(E_n - E_{n-1}) \lesssim \Gamma$, where E_n and E_{n-1} are the energies of the $4f^n$ and $4f^{n-1}$ configurations, and Γ is the Anderson hybridization energy (the width of the $4f$ level; Ref. 1, for example). The introduction of Yb atoms in the Ce crystal lattice results in an extension of the lattice (since the metallic radius of Yb^{2+} is greater than that of Ce_α) and, correspondingly, an increase in the energy gap $(E_n - E_{n-1})$. Furthermore, the appearance of Yb in the alloy leads to a decrease in Γ (since we have $\Gamma_{\text{Yb}^{2+}} \ll \Gamma_{\text{Ce}_\alpha}$, according to an estimate based on the electronic specific heat). The joint effects of the size and band factors lead to a rapid suppression of the mixed-valence state in $\text{Ce}_{0.9-x}\text{Yb}_x\text{Th}_{0.1}$.

The $\text{Yb}^{2+}\text{-Yb}^{3+}$ electronic transition appears to be a consequence of a local compression of Yb atoms which occurs in the alloy upon the $\text{Ce}_\gamma\text{-Ce}_\alpha$ transition, since the metallic radius of Ce_α is smaller than those of Yb^{2+} and Yb^{3+} ($r_{\text{Ce}_\alpha} = 1.715$ Å, $r_{\text{Yb}^{2+}} = 1.940$ Å, $r_{\text{Yb}^{3+}} = 1.740$ Å). Under this assumption, the probability for the

“production” of a Yb^{3+} atom will depend primarily on the Ce^{4+} “presses” around it.

The production of Yb^{3+} in the alloy $\text{Ce}_{0.9-x}\text{Yb}_x\text{Th}_{0.1}$ was demonstrated for an fcc lattice with random distributions of Ce^{3+} , Ce^{4+} , Yb, and Th atoms. The concentrations of Yb and Th atoms corresponded to the alloy composition $C(\text{Yb}) = x, C(\text{Th}) = 0.1$; the concentrations of Ce^{3+} and Ce^{4+} atoms were taken from the experimental composition dependence of the valence of the Ce. In the calculations we assumed that the originally divalent Yb atoms become trivalent if (1) the number of Ce^{4+} atoms in the first coordination sphere is greater than or equal to a certain critical $n_{\text{cr}}(\text{Ce})$ and (2) the trivalent Yb atoms formed as a result of the $\text{Yb}^{2+}-\text{Yb}^{3+}$ transition in turn stimulate transitions of all of the other neighboring Yb^{2+} atoms to a trivalent state.

The solid line in Fig. 2 shows results calculated for $n_{\text{cr}}(\text{Ce}) = 1$ and $n_{\text{cr}}(\text{Yb}) = 1$; the dotted line shows results calculated for $n_{\text{cr}}(\text{Ce}) = 2$ and $n_{\text{cr}}(\text{Yb}) = 1$. Note that mechanism (2) makes only a small contribution, no more than 20%. The reason is the low probability for an encounter of even two Yb atoms in a common coordination polyhedron. A further increase in $n_{\text{cr}}(\text{Ce})$ leads to a rapid decrease in the calculated valence of Yb, and even with $n_{\text{cr}}(\text{Ce}) = 3$ and $n_{\text{cr}}(\text{Yb}) = 1$ it is not possible to achieve a reasonable agreement with experiment.

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¹The apparent reason is a hysteresis in the transition: It follows from Ref. 2 that for Ce alloys with a 2% Yb impurity the temperature of the $\text{Ce}_\gamma-\text{Ce}_\alpha$ transition is ~ 40 K lower than that for the $\text{Ce}_\alpha-\text{Ce}_\gamma$ transition.

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