Valence instability of cerium in $Ce_{1-x}Th_x$

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Using the method of x-ray line shifts [O. I. Sumbaev, Usp. Fiz. Nauk 124, 281 (1978); Sov. Phys. Usp. 21, 141 (1978)], we have investigated the electronic occupation of the Ce $4f$ shell in $Ce_{1-x}Th_x$ over a wide range of composition, temperature, and pressure ($0.05 \leqslant x \leqslant 0.95$, $77 \leqslant T \lesssim 1000$ K, $0 \lesssim P \lesssim 13.5$ kbar). We observed that when $Ce_{1-x}Th_x$ undergoes the so-called $\gamma-\alpha$ transition [K. A. Gschneider, R. O. Elliot, Jr., and R. R. McDonald, J. Phys. Chem. Sol. 23, 1191 (1962)] (for $T \lesssim 150$ K or $P \gtrsim 8$ kbar) the number of cerium $4f$ electrons decreases, so that Ce in the α phase is left in the mixed-valence (MV) state. The value of the Ce valence in the MV state depends on the method of initiating the $\gamma-\alpha$ transition, and decreases as x approaches $x_{cr} \approx 0.27$. For the first time, we have determined the valence of Ce in $Ce_{1-x}Th_x$ for x in the supercritical region ($x > x_{cr}$, $T < T_{cr}$). We also found that Ce is in the MV state for x in the region $x_{cr} \lesssim x \lesssim 0.75$ and $T = 77$ K, with a valence of $\bar{m} = 3.06 \pm 0.01$ which is independent of composition. For $x \gtrsim 0.75$, $T \approx 300$ K, we observed a new electronic transition from the Ce^{3+} state to the MV state; we explain this transition by postulating the presence of a new phase (α^*) of $Ce_{1-x}Th_x$ on the $x-T$ phase diagram. At $T \approx 400$ K we observed the reversible transition $\gamma \rightleftarrows \alpha^*$. In light of this, we propose a new $x-T$ diagram for $Ce_{1-x}Th_x$. The value of the Ce mixed valence in $Ce_{1-x}Th_x$, and the reason it differs from the MV of metallic Ce, are explained on the basis of a model [V. A. Shaburov, Yu. P. Smirnov, A. E. Sovestnov, and A. V. Tyunis, Pisma Zh. Eksp. Teor. Fiz. 41, 213 (1985); JETP Lett. 41, 259 (1985)] which takes into account the final states of the $4f$ electrons associated with the MV phase.

INTRODUCTION

The closeness in energy of the inner-shell $4f$ electrons and outer conduction electrons in RE atoms can under certain circumstances lead to the appearance of the so-called mixed-valence (MV) state, see, e.g., Refs. 1,2. This state is considered to be a resonance between the energetically close states $4f^n$ and $4f^{n-1} + e$, which determine the initial and final states of a $4f$ electron.

Among the materials which exhibit MV, the metal cerium has been investigated most thoroughly; indeed, study of the physics of the MV phenomenon began with the observation of the isomorphic transition $Ce_\gamma - Ce_\alpha$ in this material. There are five known phases in Ce, at least one of which—Ce_α—has been reliably identified as an MV state. A portion of the Ce phase diagram is shown in Fig. 1(a) (Ref. 1): the γ and α phases have the FCC structure, while the α' phase has the α-uranium structure which differs only slightly from FCC. In the γ-phase, Ce is trivalent, while in the α phase it is in the MV state: according to data reported by various authors, its valence $m \approx 3.14$ to 3.67;[1,3] in the α' phase the Ce valence is close to four[1-4]. The phase equilibrium line for $Ce_\gamma - Ce_\alpha$ terminates on a critical point [Fig. 1(a), the small circle], analogous to the liquid-vapor critical point. This is one of the rare instances of a crystalline state whose phase diagram exhibits such a critical point. The electronic structure (valence) of Ce in the critical region has not been established; this fact is apparently related to the extreme experimental difficulties associated with this region ($P_{cr} \approx 18$ kbar, $T_{cr} \approx 550$ K). (As far as we know, there are no direct experimental data concerning the electronic structure of RE ions in the MV state near a critical point.

However, it is also possible to modify these electronic transitions by varying the composition of RE compounds. In the solid solutions $Ce_{1-x}Th_x$ the critical point can be observed at atmospheric pressure: $T_{cr} \approx 148$ K and $x_{cr} = 0.265$ (Ref. 5), which makes investigation of the critical behavior of the system considerably simpler. According to magnetic[6] and neutron-scattering[7] measurements, the valence of Ce in this alloy is close to three, whereas from crystallographic data, $m_{Ce_\gamma} = 3.17$ (Ref. 8). In $Ce_{1-x}Th_x$, the $\gamma-\alpha$ transition can be induced by cooling a sample down to $T < 150$ K; this transition increases the valence of Ce by 0.1 or 0.4, according to data from Refs. 7 and 8, respectively. In the region $x < x_{cr}$ and $T < T_{trans}$, the valence of Ce is found to lie between 3.5 and 3.6, i.e., the quantitative data on the electronic structure of Ce in Th alloys exhibits a spread of values. Furthermore, results were obtained in Ref. 9 from photoe-
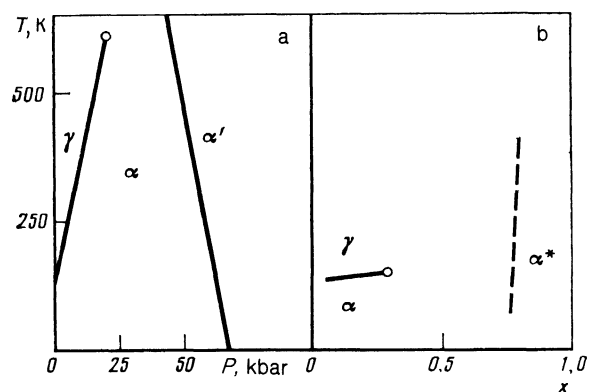

FIG. 1. Phase diagrams: (a) Ce (Ref. 1) (the body-centered δ and hexagonal β phases, in which Ce is trivalent, are not shown for simplicity); (b) $Ce_{1-x}Th_x$ (the left-hand part, $x \lesssim x_{cr}$, is taken from Ref. 5; the dotted line is the boundary of the $\gamma(\alpha)$, α^* phases). The circle marks the critical point.
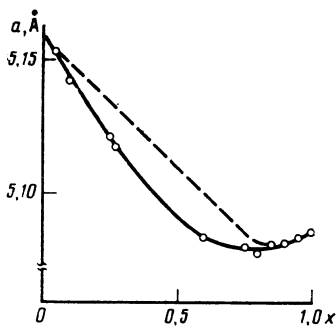
FIG. 2. Dependence of the lattice parameter of $Ce_{1-x}Th_x$ on composition (the dotted line is data from Ref. 13).

mission studies of $Ce_{1-x}Th_x$ which raise questions about the mechanism for the γ–α transition. The authors of this paper assert that because the number of $4f$ electrons (i.e., the valence) of Ce changes by 0.5 to 0.6 in this transition, the photoemission spectra of the γ and α phases should differ sharply. However, a comparison of the spectra showed that they were in fact similar for the γ and α phases, i.e., that $m_{Ce} \approx 3$. In light of this fact, the authors of Ref. 9 were led to the conclusion that the γ–α transition in $Ce_{1-x}Th_x$ could not be explained by the $4f$–(s,d) mechanism. There is no quantitative data in the literature on the electronic structure of Ce in $Ce_{1-x}Th_x$ at high pressure.

The macro- and microscopic properties of $Ce_{1-x}Th_x$ alloys have been the subject of rather detailed studies in the composition region where the isomorphic first-order phase transition occurs ($0 \lesssim x \lesssim x_{cr}$), whereas the low-Ce concentration region ($x > x_{cr}$) is left as a "white space" on the phase diagram of this system. The curve for the dependence of the lattice parameter of $Ce_{1-x}Th_x$ on composition deviates from the linear Vegard approximation (Fig. 2). According to Murao's hypothesis,[10] increasing the Th content can cause a compression of the crystal lattice, leading to an increase in the valence of Ce (compared to Ce_γ). However, magnetic susceptibility and heat capacity data on $Ce_{1-x}Th_x$[6] indicate that cerium is trivalent in the region $0.2 \leqslant x \leqslant 1$ at $T \approx 300$ K.

The purpose of this paper is to study the electronic structure (i.e., the occupation of the $4f$ shell) of Ce in $Ce_{1-x}Th_x$ by a direct microscopic method over a wide range of composition, pressures and temperatures.

EXPERIMENTAL RESULTS

The occupation of the $4f$ shell of Ce (and its variation through the electronic transition) was determined by the x-ray line shift method.[11] Because the $4f$ electron is located deep in the atom, its removal (or excitation) leads to anomalously large [compared to $6s(p)$ or $5d$ electrons] changes in energy (i.e., shifts) in the K-series of x-ray lines; $|\Delta E^{4f}_{K\alpha_{1,2}}| \approx |\Delta E^{4f}_{K\beta_{2,4}}| \approx 500$–$600$ meV, $|\Delta E^{4f}_{K\beta_{1,3}}| \approx 1500$–$1700$ meV, $|\Delta E^{6s,6p,5d}_{K\alpha,\beta}| \approx 20$–$80$ meV. The energy dependence of the "displacement-type lines" $K_{\alpha_{1,2}}$, $K_{\beta_{1,3}}$, $K_{\beta_{2,4}}$) has a characteristic V-shaped form, which is the "fingerprint" of a $4f$ electron. This feature of the x-ray line shifts allows us to identify unambiguously those events which involve $4f$ electrons.

In our experiment, we determine the change in energy

(shift) of the K-lines of Ce for a given sample of $Ce_{1-x}Th_x$ relative to a reference sample of trivalent cerium (Ce_γ); the alloy is held at liquid-nitrogen temperature, room temperature and some higher temperature ($300 < T \lesssim 1000$ K), and at high quasi-hydrostatic pressures ($0 \lesssim P \lesssim 13.5$ kbar). The difference between the number of $4f$ electrons on a Ce ion in the sample under study and in the reference sample is determined from the expression $\Delta n_{4f} = \Delta E(x,T,P)/\Delta E(Ce^{4+}\text{–}Ce^{3+})$, where $\Delta E(x,T,P)$ is the experimentally measured shift in the x-ray K-line of the sample under study, and $\Delta E(Ce^{4+}\text{–}Ce^{3+})$ is the calibrated shift corresponding to a shift in the K-line of Ce for a unit change in the number of $4f$ electrons. The quantity $\Delta E(Ce^{4+}\text{–}Ce^{3+})$ was taken from the pair of ionic compounds CeF_4–CeF_3 ($\Delta E_{K\alpha_1} = -602 \pm 12$ meV, $\Delta E_{K\beta_1} = -1727 \pm 20$ meV; see Ref. 11). It is obvious that the valence of Ce in the sample under study is $m \equiv m_{ref} + \Delta n_{4f} = 3 + \Delta n_{4f}$.

The setup for determining the x-ray line shift consists of a crystal-diffraction spectrometer of Cauchois type, with a two-meter focal length.[12] Fluorescent radiation is excited by an x-ray tube ($I = 10$ mA, $U = 150$ kV) in samples located within identical pressure chambers (cryostats, high-temperature chambers); this radiation is conveyed through a 12 mm diameter cylindrical collimator to a quartz single crystal which is bent inside cylindrical mirrors (with radii of curvature 2 m). The crystal reflection plane is $20\bar{2}3$, its thickness is 1.2 mm; the radius of curvature of the reflection planes is $k = 4.3 \times 10^{-4}$ cm^{-1} (Ref. 11). Rotation of the crystal is carried out using a precision readout apparatus. The diffraction radiation passing through a receiving slit located at the Rowland circle (of width 0.3 mm) is recorded using a scintillation detector. The sample under study and the reference sample are alternately introduced into the spectrometer's field of view; the spectrometer is then tuned to the corresponding K-line. The sought-after energy shifts $\Delta E(x,T,P)$ are calculated analytically according to the differences in the counting rates for comparable samples, and the parameters of the measured line shapes of the K-lines.

For the pressure experiments, we used "cylinder-piston" high-pressure chambers with beryllium windows. Samples in the form of fine powders were mixed with powdered polyethylene, which serves as a medium to transmit the pressure. The chamber pressure was adjusted by forward and reverse movement of the plunger. For the high-temperature measurements, vacuum chambers were used; these chambers were made of quartz with thin plane-parallel ground windows and an external heater. The sample under study consisted of a carefully blended mixture of powdered $Ce_{1-x}Th_x$ and spectroscopically pure graphite.

Solid solutions of $Ce_{1-x}Th_x$, prepared by arc melting, were single-phase, having the FCC structure, while the measured dependence of lattice parameter on composition (Fig. 2) agreed satisfactorily with the dependence obtained in Ref. 13. We investigated samples lying within the region $0.05 \leqslant x \leqslant 0.95$. In the room-temperature and low-temperature experiments, the samples were packed in special hermetically sealed containers in order to prevent oxidation; in all cases, after the basic experiments were performed we carried out an x-ray phase control to ensure the absence of $(Ce_{1-x}Th_x)O_2$.

The experimental dependences of the Ce valence on composition and external conditions in the alloys are shown
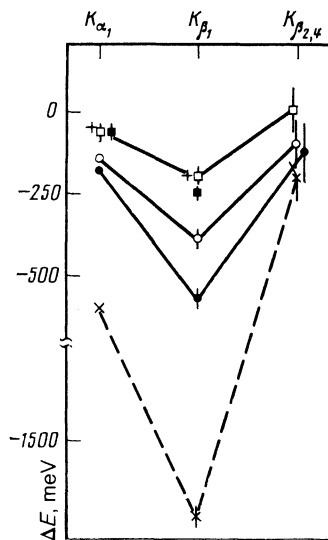
FIG. 3. Dependence of "displacement-type lines" as Ce passes into the MV state: O—metallic Ce, $P \approx 10$ kbar; ●—metallic Ce, $T = 77$ K (Ref. 14), □—$Ce_{0.95}Th_{0.05}$, $P \approx 11.5$ kbar; ■—$Ce_{0.75}Th_{0.25}$, $T = 77$ K; + — $Ce_{0.25}Th_{0.85}$, $T \approx 300$ K; ×—CeF_4-CeF_3 (Ref. 11).

FIG. 4. Dependence of the Ce valence on composition in $Ce_{1-x}Th_x$. ●, O are for $T = 77$ K and 300 K, respectively; ×—the relative volume change for the low-temperature γ-α transition in $Ce_{1-x}Th_x$ (Ref. 15).

below in Figs. 4–7. Study of the dependence of displacement-type "fingerprint lines" allows us to establish unambiguously that the change in energy of the Ce K-lines in alloys are due to partial removal of a $4f$ electron from a Ce atom. In Fig. 3 we show typical experimental "fingerprints" observed in $Ce_{1-x}Th_x$. They are analogous in sign and in their characteristic V-shape to displacements observed during the γ-α transition in metallic Ce,[14] and also in compounds with tri- and quadrivalent Ce.

Along with the electronic structure of Ce, we studied the electronic structure of Th by measuring the shift in the Th L-line for the pairs Th metal–$Th_x Ce_{1-x}$ at room temperature. We found that in all the composition regions we investigated ($0 \lesssim x \lesssim 1$), the shift in the Th L-line is close to zero, i.e., the electronic structure of Th in $Ce_{1-x}Th_x$ is the same as in the metal.

DISCUSSION OF RESULTS

In Fig. 4 we show the experimental valences of Ce in $Ce_{1-x}Th_x$ versus composition at temperatures above and below the γ-α transition temperature. It is clear that at $T = 77$ K $< T_{trans}$, the Ce is found in the MV state. In the region $x < x_{cr}$, the valence of Ce decreases smoothly from $m \approx 3.2$ ($x = 0.05$) to $m \approx 3.06$ ($x = 0.265$) and in the region $x_{cr} \lesssim x \lesssim 0.75$ (the region where the first-order phase transition changes to a second-order phase transition) the valence reaches a constant value. In the supercritical region ($x_{cr} \lesssim x \lesssim 0.75$), $\overline{m} = 3.06 \pm 0.01$. The valence of Ce at room temperature in the region $0.05 \lesssim x \lesssim 0.75$ equals $\overline{m} = 3.00 \pm 0.01$. In Fig. 4, we also present the dependence of the volume effect on composition for the γ-α transition in $Ce_{1-x}Th_x$ obtained in Ref. 15. Good agreement between the curves of $m(x)$ and of $\Delta V/V$ as a function of x is observed only in the region $x > x_{cr}$, i.e., where the first-order phase transition occurs. In the region $x > x_{cr}$, the discontinuous transition changes to a smooth one, and $\Delta V/V$ is by definition taken to be zero; nevertheless, as is clear from Fig.
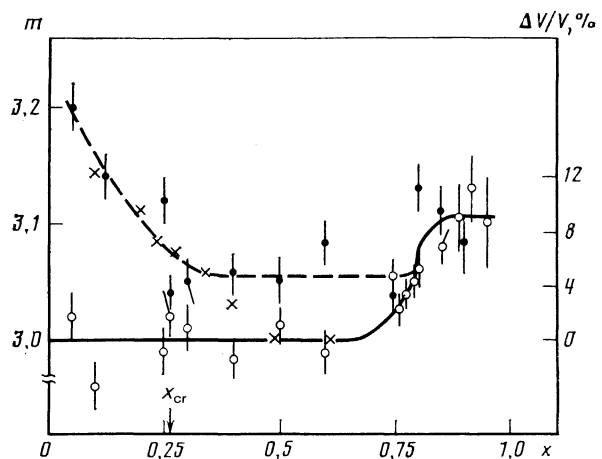
4, a change in the occupation of the $4f$ shell of Ce takes place even for the second-order phase transition.

The change in valence of Ce we observed upon cooling $Ce_{1-x}Th_x$ is quite unambiguous, see Figs. 3, 4. Therefore, the interpretation of the results of photoemission investigations of the $Ce_{1-x}Th_x$ spectra at low temperatures[9] is apparently erroneous. A likely cause of this is the fact that the real effect of a change in the Ce valence turns out to be much less than expected. Furthermore, there are two phenomena which could result in a diminished Ce valence as determined by photoemission methods; (1) the "shake-up" effect during photoionization (see, e.g., Refs. 16, 17), and (2) a stabilization effect of the lower-valence state at the surface[18] (which is the primary region examined by photoemission methods). These two mechanisms apparently cause a decrease in the true valence of Ce, so that its value is found to be beyond the limits of sensitivity of the photoemission method.

Along with the low-temperature γ-α transition in $Ce_{1-x}Th_x$, which was known earlier, in the region of high Th concentration a second electronic transition is observed, initiated by a change in the alloy composition (lattice compression); see Fig. 4, the region $0.75 \lesssim x \lesssim 0.95$. In this region, the Ce valence increases rather sharply from a value $\overline{m} = 3.00 \pm 0.01$ ($0.05 \leqslant x \lesssim 0.75$, $T \approx 300$ K) to a value of $\overline{m} = 3.11 \pm 0.02$ ($0.8 \leqslant x \leqslant 0.95$); this increase is practically independent of composition and sample temperature (77 K or 300 K). A crystallographic measurement at room temperature showed that this transition is isomorphic. Therefore, the conclusion reached by the authors of Ref. 6, i.e., that the valence of Ce does not change in the range $0.2 \leqslant x \leqslant 1$, $T \approx 300$ K, is incorrect. In this paper, the magnetic susceptibility was measured over a wide range of compositions. The thorium-rich region was studied only at $x = 0.7$ and 1; therefore, the transition Ce^{3+}-Ce^{MV} at $x \approx 0.75$ was omitted by chance.

The observed jump in the valence of Ce can be explained by the supposition that in the region $x \gtrsim 0.75$ there is a phase (which we call α^*) in which Ce is in the MV state; then crossing the γ-α^* phase boundary gives rise to the observed change in m. Under this hypothesis, the x-T phase diagram of $Ce_{1-x}Th_x$ resembles the P-T phase diagram of metallic
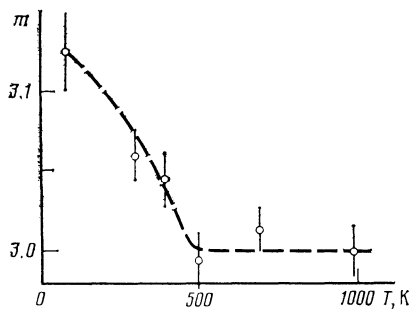
FIG. 5. Temperature dependence of the valence of Ce in $Ce_{0.2}Th_{0.8}$.

Ce, Fig. 1; they differ, however, in that the "high-pressure" phases—α' for Ce_{met} and α^* for Ce_{alloy}—have substantially different valences (≈ 4 and ≈ 3.11, respectively).

It is clear from Fig. 4 that the $\gamma-\alpha^*$ transition takes place within a narrow range of x, and the boundary of the transition is practically independent of temperature. This indicates that the phase boundary is rather steep (dT/dx is 20–40 K/%Th). If the slope of the $\gamma-\alpha^*$ phase boundary is positive, we might expect that, under heating, a sample from the α^* phase region undergoes an $\alpha^*-\gamma$ transition as it crosses the phase boundary. The data shown in Fig. 5 confirm this hypothesis: under heating, a sample of $Ce_{0.2}Th_{0.8}$ undergoes an electronic transition—a rapid decrease in the Ce valence. The transition is invertible: when the sample is cooled to room temperature, the valence returns to its original value. The $\alpha^*-\gamma$ transition temperature (the temperature at which Ce in the α^* phase passes into the trivalent γ phase) corresponds to ≈ 400 K. The valence of Ce in $Ce_{0.2}Th_{0.8}$ in the range $500 \lesssim T \lesssim 1000$ K equals $\bar{m} = 3.01 \pm 0.01$. Control measurements for samples located to the left of the $\gamma-\alpha^*$ phase boundary in composition show that Ce remains trivalent across the entire range of investigation, i.e., $300 \lesssim T \lesssim 1000$ K.

The difference between the γ and α^* phases of $Ce_{1-x}Th_x$ can be observed visually. Samples from the range $0 \lesssim x \lesssim 0.75$ darken rapidly (in the course of a few hours) once they have converted to oxide, whereas samples from the region $x > 0.75$ remain shiny, and can be kept in air for long periods of time without change. This is confirmed both by x-ray phase analysis and data from x-ray line shifts. This behavior does not seem surprising, if we assume that a γ-phase atom of Ce which is "free" to form a chemical bond with oxygen becomes "bound" in the α^* phase due to fluctuations between the states $4f^1$ and $4f^0$, e.

What initiates the $\gamma-\alpha^*$ transition is apparently the so-called "internal compression", which arises in the $Ce_{1-x}Th_x$ lattice when atoms of Ce are replaced by atoms of Th which are smaller in size. Why, however, does this "internal compression" not initiate the $\gamma-\alpha$ transition? We assume that the MV state comes about when the condition $|E_n-E_{n-1}| \lesssim \Gamma$ is fulfilled, where E_n and E_{n-1} are the energies of the $4f^n$ and $4f^{n-1}$, e configurations, respectively, and Γ is the Anderson hybridization energy (the width of the $4f$ level), see, e.g., Ref. 2. Under applied pressure (in our case due to the introduction of Th atoms into the Ce lattice) the $4f$ level approaches the bottom of the conduction band, i.e., E_n-E_{n-1} decreases. On the other hand, the presence of Th in the alloy can lead to a decrease in the density of states
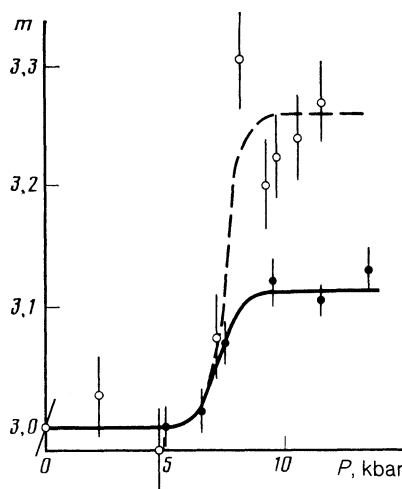
at the Fermi level, i.e., a decrease in Γ. The competition between these two factors—size and banding—will also determine, in the final analysis, the condition for a transition to the MV state: for low Th concentrations, the "internal compression" is insufficient and the banding factor prevails; for large x the size factor outweighs the band factor and we observe the $\gamma-\alpha^*$ transition.

The $\gamma-\alpha$ transition in Ce–Th alloys can also be inititated by using high pressure ($P \gtrsim 8$ kbar). According to data from Gschneider et al.,[15] the volume effect across the transition decreases as we approach the critical concentration ($x_{cr} \approx 0.31$), above which a first-order phase transition becomes a second-order phase transition. The effect of pressure on the valence of Ce in $Ce_{1-x}Th_x$ investigated in this paper is shown in Figs. 6 and 7. In Fig. 6, we show a typical dependence of the Ce valence on pressure for samples from the region $x < x_{cr}$. It is clear that in the neighborhood of $P \approx 7$ kbar, m increases rather rapidly (i.e., undergoes a $\gamma-\alpha$ transition) while for $P \approx 9$ kbar it reaches saturation. The dependence $m(P)$ for $Ce_{1-x}Th_x$ is similar to that of metallic Ce (the dotted curve in Ref. 6).[1)] The effect of composition on the degree of valence change of Ce in alloys after the transition to the α phase ($P \approx 11$ kbar) is shown in Fig. 7. A smooth decrease in m is observed as the critical concentration is approached: the dependence $m(x)$ in the region
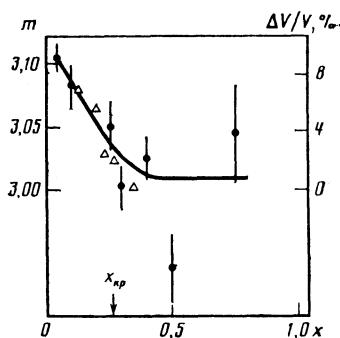

FIG. 6. Pressure dependence of the valence of Ce in $Ce_{0.95}Th_{0.05}$ ($\bullet$) and in metallic Ce (O) (Ref. 14).

FIG. 7. Dependence on composition of the Ce valence for $P \approx 11.5$ kbar ($\bullet$) and of the relative volume change for the $\gamma-\alpha$ transition ($\triangle$) (Ref. 15) in $Ce_{1-x}Th_x$.

$x < x_{cr}$ correlates well with the dependence of $\Delta V/V$ on x obtained in Ref. 15—i.e., the triangles in Ref. 7.

It is clear from Figs. 4 and 7 that the absolute change in the valence of Ce, and also $\Delta V/V$ in the course of the γ–α transition for $Ce_{1-x}Th_x$, depend on the method of initiating the transition. Cooling produces an effect 1.5 times larger than applying pressure. An analogous situation also obtains for metallic Ce;[14] furthermore, the change in valence for "pure" Ce upon entering the α phase is found to be 2.5 times larger than for alloyed material.

In Ref. 19 it was observed that cerium has a valence of ≈ 3.13, ≈ 3.27 or ≈ 3.39 in MV compounds. This result was explained by associating the different valence values with different $4f$ electron final states which enter into the formation of the MV state: the conduction band (or valence band of a ligand), and the localized $6s(p)_{1/2}$ and $5d(6p)_{1/2}$ states ($m_{calc} = 3.14$, 3.25 and 3.40, respectively). Starting from this, we can view the electronic structure of α- and α^*–Ce in $Ce_{1-x}Th_x$ as a resonance (fluctuation) between the states $Ce^{3+}, 4f^1$ and $Ce^{4+}, 4f^0$, i.e., a $4f$ electron is injected into the conduction band in the course of forming the MV state.[2] Analogously, the low-temperature α-modification of metallic Ce can be considered a resonance state of Ce^{3+}, $4f^1$ and Ce^{4+}, $5d_{3/2}$; the high-pressure phase can be considered a resonance of Ce^{3+}, $4f^1$ and Ce^{4+}, $6s(p)_{1/2}$.

The difference in magnitudes of the valences of low-temperature and compressed Ce (both in the metal and in the alloys) can also be explained by the fact that the experiments using pressure were carried out at room temperature. In Ref. 13 it was shown that an increase in temperature decreases the Ce valence in MV compounds; therefore it is not impossible that the valence of Ce increases and becomes comparable to that of the low-temperature modification if the γ–α transition is induced by pressure at decreased temperatures ($T < 300$ K).

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[1] All the data on the valence of metallic Ce obtained in Ref. 14 from calibrations using CeO_2–CeF_3 are recalculated in this paper for calibration shifts from CeF_4–CeF_3 (Ref. 11).

[2] For small x and $T = 77$ K, we do not exclude the variant Ce^{3+}, $4f^1$– Ce^{4+}, $6s(p)_{1/2}$.

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