Double 4*f*-collapse in the isomorphic Ce_γ–Ce_α phase transition in $Ce_{0.9-x}R_xTh_{0.1}(R=Eu,Yb)$

V. A. Shaburov, A. E. Sovestnov, Yu. P. Smirnov, A. V. Tyunis, and S. I. Sinyakova

B. P. Konstantinov St. Petersburg Institute of Nuclear Physics, Russian Academy of Sciences, 188350 Gatchina, Leningrad Oblast, Russia

(Submitted 4 October 1993)
Zh. Eksp. Teor. Fiz. **105**, 439–446 (February 1994)

The population of the 4*f* shell of Ce, Eu, and Yb in $Ce_{0.9-x}Eu_xTh_{0.1}(0.01<x<0.05)$ and $Ce_{0.9-x}Yb_xTh_{0.1}$ $(0.04<x<0.20)$ is investigated by the method of x-ray shifts.[8] It is found that in the isomorphic Ce_γ–Ce_α phase transition[1,2] induced by cooling of samples $(T=77$ K) in the range $x<0.015$ and $x<0.04$ for the alloys with Eu and Yb, respectively, a simultaneous temperature-reversible decrease occurs in the number of 4*f* electrons (an increase in the valency) of Ce, Eu, and Yb, viz., there are electronic transitions from the trivalent state of Ce $(m_{Ce}=3.00\pm0.01)$ and the divalent states of Eu $(m_{Eu}=2.02\pm0.02)$ and Yb $(m_{Yb}=1.99\pm0.02)$ to states with noninteger valencies $m'_{Ce}=3.20\pm0.01$ and 3.12 ± 0.01 (for the alloys with Eu and Yb, respectively), $m'_{Eu}=2.51\pm0.06$, and $m'_{Yb}=2.42\pm0.05$. It is postulated that the $Eu^{2+}(Yb^{2+})$–$Eu^{3+}(Yb^{3+})$ transition is due to the local compression of the Eu (Yb) atoms that arises in the lattice in the Ce_γ–Ce_α transition.

INTRODUCTION

The anomalous behavior of the crystal lattice of metallic cerium observed at high pressure ($P\sim8$ kbar) by Bridgman[1] and at low temperature ($T<160$ K) by Trombe[2] is a phenomenon that has given rise to a new class of transformations in crystalline solids—isomorphic phase transitions. The feature that distinguishes this phenomenon from ordinary structural transitions in crystals is the preservation of the symmetry of the lattice (the isostructural character): the compressed (and low-temperature) phase (Ce_α) is similar to the normal phase (Ce_γ). Both phases are face-centered cubic ($d_\gamma=5.16$ Å, $d_\alpha=4.81$ Å, according to Ref. 3). This behavior of the crystal lattice is due to the closeness in energy of the inner, localized 4*f* electrons and outer, valence 5*d* and 6*s* electrons of Ce. Under certain external conditions (pressure, temperature), a transition is possible from the "normal" trivalent state ($Ce^{3+}4f^1,5d6s^2$) to a state of so-called intermediate valency (see, e.g., Refs. 4 and 5),[1)] i.e., the phenomenon here occurs not on the lattice level but on the intra-atomic level, and consists in a rearrangement of the electron shell of the atoms (transition of the 4*f* electron into the valence shell or band), accompanied by a sharp ($\approx17\%$) decrease (collapse) of their volume.

The characteristics of the Ce_γ–Ce_α transition (temperature, pressure, type of transition, volume effect, etc.) that are important for understanding the physical meaning of intermediate valency can be controlled if we introduce impurities of other elements into the Ce lattice. However, the microscopic properties of Ce in such matrices (population of the 4*f* shell, degree of removal of the 4*f* electron from the atom in the isomorphic transition, etc. have not been thoroughly studied, and to our knowledge, there are no direct experimental data on the electronic structure of an impurity atom embedded in the lattice.

Of all the rare-earth elements, Eu and Yb exert the greatest influence on the Ce_γ–Ce_α transition.[6,7] The "doping" of Ce by small admixtures (a few percent) of Eu and Yb sharply reduces the volume effect, while the transition temperature decreases anomalously rapidly with rising impurity concentration, and so on.

The aim of our work is to investigate by a direct microscopic method the electronic structure (population of the 4*f* shell) of Ce, Eu, and Yb in $Ce_{0.9-x}R_xTh_{0.1}$ (R=Eu, Yb) in the "normal" phase (Ce_γ) and collapsed phase (Ce_α). The addition of thorium to the Ce–Eu(Yb) system prevents the formation of the hexagonal phase (β–Ce) at low temperature.[6]

EXPERIMENTAL RESULTS

The population of the 4*f* shell of Ce, Eu, and Yb (and its variation during the transition) was determined by the method of shifts of x-ray lines.[8] Because of the position of the 4*f* electron deep in the atom, its removal (or excitation) leads to an anomalously large (in comparison with the 6*s*(*p*) and 5*d* electrons) change (shift) in the energies of the x-ray lines of the *K* series: $|\Delta E^{4f}_{K_{\alpha_{1,2}}}|\approx500$–$600$ meV, $|\Delta E^{4f}_{K_{\beta_{1,3}}}|\approx1500$–$1700$ meV, $|\Delta E^{6s(p),5d}_{K_{\alpha,\beta}}|\approx20$–$80$ meV. This feature of the effect makes it possible to identify unambiguously events involving the participation of 4*f* electrons.

In the experiment, the differences (shifts) ΔE of the energies of the K_{β_1} line of Ce and the K_{α_1} lines of Eu and Yb in the sample investigated, maintained at $T=300$ K and $T=77$ K, from those in a reference sample (metallic Ce, Eu, and Yb) were measured. The differences in the number of 4*f* electrons per Ce, Eu, and Yb ion in the investigated sample and reference sample were determined as $\Delta n_{4f}=\Delta E/\Delta E(f^n-f^{n-1})$, where $\Delta E(f^n-f^{n-1})$ is the calibration shift corresponding to the shift of the *K* line

1063-7761/94/020235-04$10.00

upon a change in the number of $4f$ electrons by unity. It is obvious that the valency $m=m_0+\Delta n_{4f}$, where m_0 is the valency in the reference sample.

The experimental values of $\Delta E(f^n-f^{n-1})$ were taken for the following pairs of ionic compounds: CeF_4–CeF_3, EuF_3–EuF_2, and Yb_2O_3–YbS ($\Delta E_{K_{\beta_1}}^{\text{Ce}}=-1727\pm20$ meV, $\Delta E_{K_{\alpha_1}}^{\text{Eu}}=-631\pm15$ meV, $\Delta E_{K_{\alpha_1}}^{\text{Yb}}=-568\pm7$ meV).

Solid solutions $Ce_{0.9-x}R_xTh_{0.1}$, prepared by the method of arc melting, were single-phase, with the fcc structure, and the lattice parameter in the investigated range of compositions increased essentially linearly with increasing x (see the inserts in Figs. 2 and 3). Since metallic Eu and Yb have relatively high vapor pressures (in comparison with Ce and Th), and in the synthesis the initial charge is observed to be appreciably depleted in these components,[6] the true composition of the synthesized materials was determined by fluorescence analysis. The samples investigated were tablets pressed from a mixture of the working substance and polyethylene as a filler, and packed (to prevent oxidation) in special hermetic aluminum containers; after the basic experiments, x-ray-phase monitoring was performed to confirm the absence of oxides of Ce, Eu, and Yb.

The apparatus for determining the shifts of the x-ray lines is a Cauchois crystal-diffraction spectrometer with a two-meter focal length.[9] Fluorescent emission in samples placed in identical cryostats, one of which is filled with liquid nitrogen, is excited by an x-ray tube ($I=10$ mA, $U=140$ kV) and, through a cylindrical collimator of diameter 12 mm, is incident on a quartz single crystal bent to give cylindrical mirrors (with radius of curvature equal to 2 m; the reflecting planes are $20\bar{2}3$ planes, the thickness is 1.8 mm, and the coefficient of bending of the reflecting planes[8] is $K=4.3\times10^{-4}$ cm^{-1}). The crystal is rotated by means of a precision measuring device. The diffracted radiation that has passed through the receiving slit (of width 0.3 mm) located on the focal circle is detected by a scintillation detector. For each position of the crystal, the sample under investigation and reference sample are introduced alternately into the field of view of the spectrometer, which is tuned to the corresponding K-line. The energy shift $\Delta E(x,T)$ is calculated analytically from the difference of the count rates for the samples being compared, and the parameters of the profile of the K-line being measured.

The temperature T_c of the Ce_γ–Ce_α transition in the Ce–Eu–Yb alloys decreases rapidly with increasing concentration of Eu and Yb (see the insert in Fig. 1), and even for a small concentration ($\approx$2–4 at.%), cooling of the sample to $T=77$ K (the lower temperature limit of our spectrometer) is not sufficient to induce the transition.[7] However, it is possible to preserve the collapsed state (the Ce_α phase) in the region $x\lesssim0.04$ even at $T=77$ K if we note that the Ce_γ–Ce_α transition has hysteresis: the transition temperature $T_c(\gamma\rightarrow\alpha)$ for a sample undergoing cooling is 40 K lower than the transition temperature $T_c(\alpha\rightarrow\gamma)$ for a sample undergoing heating (Ref. 6). In a low-temperature experiment, the Ce-Eu alloys investigated were cooled to $T=4.2\text{ K}<T_c$ and transferred to the working cryostat with liquid nitrogen; the Ce–Yb alloys from the range of compositions $x\geqslant0.04$ were subjected to the same procedure.[2)]

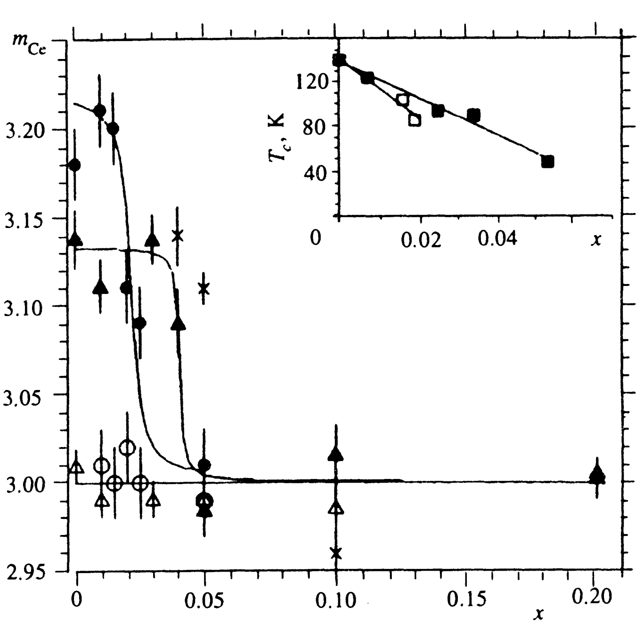

FIG. 1. Experimental dependence of the valency of Ce in $Ce_{0.9-x}Eu_xTh_{0.1}$ and $Ce_{0.9-x}Yb_xTh_{0.1}$ on the composition; the points ○ and △ ($T=300$ K) and ● and ▲ ($T=77$ K) pertain to the alloys with Eu and Yb, respectively; the points × are for $T=77$ K after cooling of the alloys with Yb to $T=4.2$ K. The insert is the (T_c, x) phase diagram (the points □ are for $Ce_{0.9-x}Eu_xTh_{0.1}$ and the points ■ are for $Ce_{0.9-x}Yb_xTh_{0.1}$), obtained in Ref. 7.

Figures 1–3 show the experimental valencies of Ce, Eu, and Yb in the investigated alloys as a function of the composition for $T=300$ K and $T=77$ K. It can be seen from Fig. 1 that cooling of samples of $Ce_{0.9-x}R_xTh_{0.1}$ (R=Eu,Yb) with $x_{\text{Eu}}\leqslant0.015$ and $x_{\text{Yb}}\leqslant0.04$ initiates an electronic transition from the trivalent state (light points and triangles) to a state of intermediate valency (dark points and triangles), similar to the Ce_γ–Ce_α transition in metallic Ce (see, e.g., Ref. 8). "Doping" of Ce with small (2–4 at.%) admixtures of Eu and Yb leads to suppression of the Ce_γ–Ce_α transition: For $x\gtrsim0.015$ in $Ce_{0.9-x}Eu_xTh_{0.1}$ and $x\gtrsim0.04$ in $Ce_{0.9-x}Yb_xTh_{0.1}$ we observe a sharp decrease in the valency of Ce from the values $\bar{m}_{\text{Ce(Eu)}}$ $(x\lesssim0.015)=3.20\pm0.01$ and $\bar{m}_{\text{Ce(Yb)}}$ $(x\lesssim0.04)=3.12\pm0.01$ to $\bar{m}_{\text{Ce(Eu,Yb)}}$ $(x\gtrsim0.05)=2.98\pm0.01$ (Fig. 1). The valency of Ce in the γ phase is equal to $\bar{m}_{\text{Ce(Eu,Yb)}}$ (x=0–0.2, $T=300$ K$)=3.00\pm0.01$.

Simultaneously with the $4f$ collapse in the Ce atom, we observe $4f$ collapse in the Eu and Yb atoms (the dark points and triangles in Figs. 2 and 3). In the Ce_γ–Ce_α transition, at the same critical concentrations as for Ce, the initially bivalent Eu and Yb atoms in $Ce_{0.9-x}Eu(Yb)_xTh_{0.1}$ [$\bar{m}_{\text{Eu}}$ (x=0.01–0.05, $T=300$ K$)=2.02\pm0.02$, $\bar{m}_{\text{Yb}}$ (x=0.04–0.2, $T=300$ K$)=1.99\pm0.02$] go over discontinuously into a state with noninteger valency with values $\bar{m}_{\text{Eu}}$ $(x\lesssim0.015,\ T=77\text{ K})=2.51\pm0.06$ and $\bar{m}_{\text{Yb}}(x\lesssim0.04,\ T=77\text{ K})=2.42\pm0.05$.

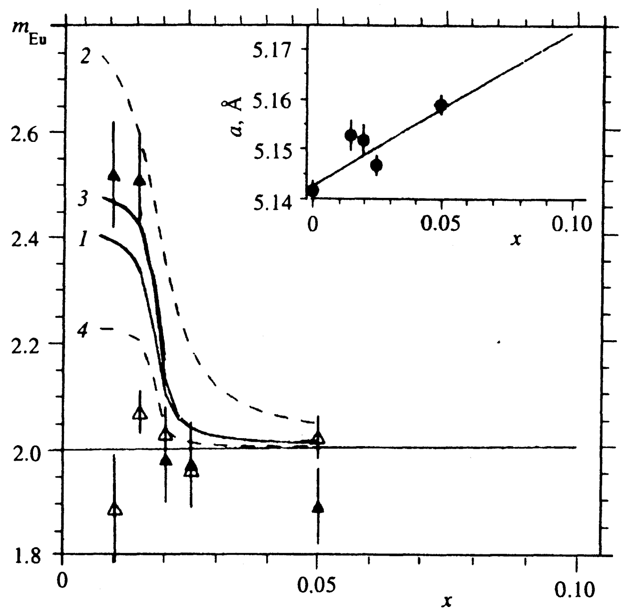

FIG. 2. Experimental valency of Eu in $Ce_{0.9-x}Eu_xTh_{0.1}$ as a function of the composition; the points Δ are for $T=300$ K, and the points ▲ for $T=77$ K. The curves *1* and *2* are calculated from Eqs. (1) and (2) for $n_{cr}=3$ and $n_{cr}=2$, respectively. The curves *3* and *4* are calculated from Eqs. (1), (2), and (3), for $n_{cr}=3$ and $n_{cr}=4$, respectively. The insert shows the dependence of the lattice parameter in $Ce_{0.9-x}Eu_xTh_{0.1}$ on composition ($T=300$ K).

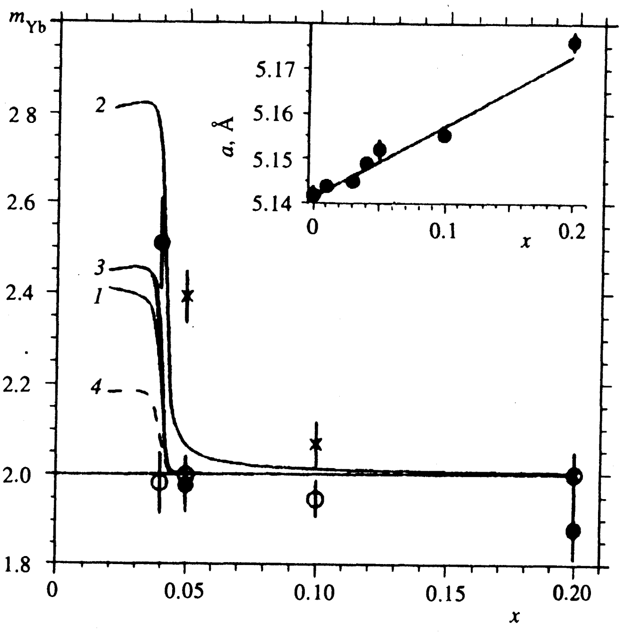

FIG. 3. Experimental dependence of the valency of Yb in $Ce_{0.9-x}Yb_xTh_{0.1}$ on composition; the points ○ are for $T=300$ K, the points ● are for $T=77$ K, and the points × are for $T=77$ K after cooling of the samples to $T=4.2$ K. The curves *1* and *2* are calculated from Eqs. (1) and (2) for $n_{cr}=2$ and $n_{cr}=1$, respectively. The curves *3* and *4* are calculated from Eqs. (1), (2), and (3), for $n_{cr}=2$ and $n_{cr}=3$, respectively. The insert shows the dependence of the lattice parameter in $Ce_{0.9-x}Yb_xTh_{0.1}$ on composition ($T=300$ K).

The phenomenon of simultaneous change of valency in Ce, Eu, and Yb in $Ce_{0.9-x}Eu(Yb)_xTh_{0.1}$ is temperature-reversible.

The value of the valency of Ce and Yb in the alloy in the neighborhood of the critical concentration ($x_{cr}\approx 0.05$) also depends on the previous history of the sample. For example, for a $Ce_{0.85}Yb_{0.05}Th_{0.1}$ sample cooled to $T=4.2$ K and then heated to $T=77$ K, we had $m_{Ce}(77\text{ K})=3.11\pm 0.01$ and $m_{Yb}(77\text{ K})=2.39\pm 0.05$, whereas for the same sample cooled from $T=300$ K to $T=77$ K we had $m_{Ce}(77\text{ K})=2.98\pm 0.02$ and $m_{Yb}(77\text{ K})=1.98\pm 0.05$ (the crosses and dark points in Figs. 1 and 3) the small concentration shift in the boundary of the transition is probably associated with the hysteresis of the transition).

DISCUSSION

The suppression of the Ce_γ–Ce_α transition in $Ce_{0.9-x}Eu(Yb)_xTh_{0.1}$ by europium and ytterbium can be understood qualitatively from the following considerations. The intermediate-valency state of Ce in the α phase is usually explained as the result of the rapid fluctuations that arise between the energetically close $4f^1$ and $4f^0$ states when $E_{ex}/\Gamma \lesssim 1$, where $E_{ex}=E_{4f^0}-E_{4f^1}$ is the energy difference between the $4f^0$ and $4f^1$ states, and Γ is the energy of hybridization of a $4f$ electron with an electron of the conduction band (see, e.g., Ref. 5). Introduction of Eu and Yb atoms into the cerium crystal lattice leads to dilatation of the lattice, since the metallic radii of Eu^{2+} and Yb^{2+} are greater than the metallic radius of Ce[$r_{Ce}=1.715$ Å, $r_{Eu^{2+}}=2.042$ Å, and $r_{Yb^{2+}}=1.940$ Å (Ref. 10)], and, correspondingly, to an increase in the energy gap E_{ex}. In addition, the appearance of Eu and Yb atoms in the alloy leads to a decrease in the value of Γ, since Γ is proportional to the electronic specific heat γ, and $\gamma_{Eu^{2+}}=2.8 \lesssim \gamma_{Yb^{2+}}=2.9 \ll \gamma_{Ce}=58\text{ mJ/g}\cdot\text{atom}\cdot\text{K}^2$ (Ref. 11).

The joint action of the size and band factors that increases the ratio E_{ex}/Γ also leads to rapid suppression of the fluctuation in $Ce_{0.9-x}Eu(Yb)_xTh_{0.1}$. Since $r_{Eu^{2+}} > r_{Yb^{2+}}$ and $\Gamma_{Eu^{2+}} \lesssim \Gamma_{Yb^{2+}}$, the Ce_γ–Ce_α transition in the alloys with europium should be suppressed more "energetically" than in the alloys with Yb, and this is observed in experiment: $x_{cr}^{Eu}\approx 0.015$ is less than $x_{cr}^{Yb}\approx 0.04$ (Fig. 1).

The Eu^{2+}–Eu^{3+} (Yb^{2+}–Yb^{3+}) electronic transition that occurs simultaneously with the Ce^{3+}–Ce^{4+} transition in the alloys is likely to be due to the local compression of the Eu and Yb atoms in the Ce_γ–Ce_α transition, since the metallic radius of Ce_α is smaller than the metallic radii of Eu^{2+} and Yb^{2+}. Making that assumption, the probability of "creation" of trivalent Eu and Yb atoms will depend primarily on the Ce^{4+} atoms that surround them and give rise to the compression.

The process of "creation" of Eu^{3+} and Yb^{3+} in the $Ce_{0.9-x}Eu(Yb)_xTh_{0.1}$ system has been demonstrated for a face-centered cubic lattice with a random distribution of Ce^{3+}, Ce^{4+}, Eu(Yb), and Th atoms. Assuming that the electronic transition in Eu and Yb occurs when the number of Ce^{4+} ions in their first coordination polyhedron becomes equal to or greater than a certain critical number

($n > n_{cr}$), one can show[5] that the probability of "creation" of Eu^{3+} (Yb^{3+}) will be equal to

$$P_0^{Eu(Yb)}(x) = \sum_{n=n_{cr}}^{12} \frac{12!}{n!(12-n)!} C_0^n (1-C_0)^{12-n}, \qquad (1)$$

where 12 is the coordination number for the face-centered cubic cell and $C_0 = (0.9-x)\,[m_{Ce}(x)-3]$ is the concentration of Ce^{4+}, $m_{Ce}(x)$ being the valency of Ce in the alloy. It is obvious that

$$m_{Eu(Yb)}(x) = 2 + P_0^{Eu(Yb)}(x). \qquad (2)$$

The valencies of Eu and Yb calculated from Eq. (2) as a function of the composition of the alloys are shown in Figs. 2 and 3 (curves *1* and *2*, corresponding to $n_{cr}=3$ and $n_{cr}=2$ for Eu, and $n_{cr}=2$ and $n_{cr}=1$ for Yb), and, as can be seen from the figures, agree well with the experimental data.

Thus, a rather simple mechanism in which the quadrivalent Ce atoms formed in the Ce_γ–Ce_α transition initiate a valency transition in their bivalent nearest neighbors provides a reasonable description of the change of valency of the Eu and Yb in the $Ce_{0.9-x}Eu(Yb)_xTh_{0.1}$ alloys that we have investigated.

This mechanism can be regarded as a zeroth approximation. Since the metallic radii $r_{Eu^{3+}} = 1.799$ Å and $r_{Yb^{3+}} = 1.740$ Å (Ref. 10) are smaller than the radii $r_{Eu^{2+}}$ and $r_{Yb^{2+}}$, respectively, it is logical to assume that the Eu^{3+} and Yb^{3+} atoms formed in the transition can act on their Eu^{2+} (Yb^{2+}) nearest neighbors in the same way as the Ce^{4+} atoms. (This additional mechanism has a dynamical character and can be calculated by an iterative method. However, because of the small number of Eu (Yb) atoms in the region of the electronic transition ($x \lesssim 0.04$), two or three iterations are sufficient for the valency $m_{Eu(Yb)}$ to reach saturation.)

The probability of "creation" of Eu^{3+} (Yb^{3+}) atoms, with the primary and supplementary mechanism taken into account, was calculated using Eq. (1) and the following expression for the concentration of all atoms giving rise to the compression:

$$C = (0.9-x)[m_{Ce}(x)-3] + x[m^i_{Eu(Yb)}(x)-2], \qquad (3)$$

where $i \gtrsim 0$ labels the iteration. The calculated curves *3* ($n_{cr}=3$ and 2, respectively, for Eu and Yb) are given in Figs. 2 and 3. Comparing with the curves *1* (the primary mechanism) and *b* (the primary plus the supplementary mechanism), it can be seen that the contribution of the supplementary mechanism is small (~10–20%) and lies essentially within the limits of the experimental error in the determination of the valency. This is due to the small total number of Eu and Yb atoms in the alloys in which the electronic transition is observed. The best agreement between the experimental data and the calculation is obtained (with the primary and supplementary mechanisms taken into account) with $n_{cr}=3$ for Eu and $n_{cr}=2$ for Yb. Further increases in n_{cr} lead to a rapid decrease in the calculated value of the valency of Eu and Yb, and in the case $n_{cr}=4$ for alloys with Eu and $n_{cr}=3$ for alloys with Yb, it is no longer possible to obtain reasonable agreement with experiment (curves *4* in Figs. 2 and 3).

In conclusion, we note that the observed phenomenon of simultaneous change of the valencies of different atoms constituting a multicomponent system can be regarded as a new type of electronic transition.

The authors thank O. I. Sumbaev for his sustained interest in the work and for discussions, B. V. Grigor'ev and E. G. Andreev for help in the experiment, and P. L. Sokolov for design assistance.

The work was carried out under the auspices of project No. 93-02-3236, supported by the Fundamental Research Fund of the Russian Academy of Sciences.

[1] The intermediate-valency state can be regarded as a resonance between the energetically close states $4f^n$ and $4f^{n-1}+e$ determined by the initial and final states of the $4f$ electron.

[2] For alloys of Ce with Yb in the range $x \lesssim 0.4$, the temperature T_c is higher than 77 K, and therefore, to initiate the Ce_γ–Ce_α transition, it is sufficient to cool the sample to $T=77$ K.

---

[1] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **58**, 166 (1923).

[2] F. Trombe, C. R. Acad. Sci. **198**, 1591 (1934).

[3] K. A. Gschneidner Jr., *Rare Earth Alloys* (Van Nostrand, Princeton, N. J., 1961) [Russ. transl., Mir, Moscow, 1965].

[4] J. M. Robinson, Phys. Rep. **51**, 1 (1979).

[5] D. I. Khomskiĭ, Usp. Fiz. Nauk **129**, 443 (1979) [Sov. Phys. Usp. **22**, 879 (1979)].

[6] K. A. Gschneidner Jr., R. O. Elliott, and R. R. McDonald, J. Phys. Chem. Solids **23**, 1201 (1962).

[7] M. A. Manheimer and R. D. Parks, in *Valence Instabilities and Related Narrow-Band Phenomena* (R. D. Parks, ed.) (Plenum Press, New York, 1977), p. 447.

[8] O. I. Sumbaev, Usp. Fiz. Nauk **124**, 281 (1978) [Sov. Phys. Usp. **21**, 141 (1978)].

[9] V. A. Shaburov *et al.*, Zh. Eksp. Teor. Fiz. **65**, 1157 (1973) [Sov. Phys. JETP **38**, 573 (1974)].

[10] W. B. Pearson, *The Crystal Chemistry and Physics of Metals and Alloys* (Wiley, New York, 1972) [Russ. transl., Mir, Moscow, 1977].

[11] K. A. Gschneidner Jr., Solid State Phys. **16**, 275 (1964).

Translated by P. J. Shepherd