**REVIEWS OF TOPICAL PROBLEMS** 

**Contents** 

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### The puzzle of the $\gamma \rightarrow \alpha$ and other phase transitions in cerium

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<u>Abstract.</u> We discuss recent research on phase transitions in cerium under pressure, including new experiments on the  $\gamma \rightarrow \alpha$  transition, which indicate that it is a hidden structural phase transition. We also discuss some models of relevance to the field, both theoretical and computational.

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#### 1. Introduction

Cerium was discovered in 1803 simultaneously in Sweden and Germany. It was named after the dwarf planet Ceres found two years earlier [1]. (Currently, Ceres is the largest and most massive body in the asteroid belt, and contains almost a third (32%) of the total mass of the belt.) Cerium is the most abundant (about 0.0046–0.0068% of Earth's crust by weight) and least expensive of the rare earth elements. Nowadays, cerium is widely used for commercial applications. In the form of cerium oxide, for example, it is added to fuel to reduce emissions and to glass and enamels to change their color, while in the form of flint (iron-cerium alloy), it is used in lighters. Cerium oxide (CeO<sub>2</sub>) is also an important component of glass polishing powders and phosphors used in screens and fluorescent lamps.

But from the fundamental physics standpoint, cerium is most interesting because of its unusual electronic structure, which manifests itself in the phase polymorphism of its condensed state [2]. Seven allotropic phases of cerium are currently distinguished:  $\alpha$  (cubic),  $\beta$  (double hexagonal close packed, dhcp [3]),  $\gamma$  (face-centered cubic, fcc, *Fm3m*),  $\delta$  (bodycentered cubic, bcc [4]),  $\alpha'$  (C-type orthorhombic [5, 6] or the  $\alpha$ -U structure),  $\alpha''$  (C2/*m* monoclinic [7, 8]), and  $\varepsilon$  (bodycentered tetragonal, bct, *I*2/*m* [9, 10]). (See Tables 1, 2 and Fig. 1.) It is also worth noting that the density of the liquid phase is higher than the density of the bulk  $\delta$  phase. In

Phase	Crystal structure	Space symmetry	Lattice parameters, A	Conditions, Reference
α	Cubic	$Pn\bar{3}m$ , $Pa\bar{3}$ (see Sections 6, 7)	<i>a</i> = 4.824	P = 0.81 GPa, room $T[15]$
β	Double hexagonal close packed (dhcp)	<i>P</i> 6 <sub>3</sub> / <i>mmc</i>	a = 3.6810 c = 11.857	$P = 0, \operatorname{room} T[16]$
γ	Face-centered cubic (fcc)	Fm3m	a = 5.1610	$P = 0, \operatorname{room} T[16]$
δ	Body-centered cubic (bcc)	Fm3m	<i>a</i> = 4.11	P = 0, T = 1041  K [2, 4]
α′	α-U structure: C-centered (based) orthorhombic	Cmcm	a = 3.0143(2) b = 5.8935(3) c = 5.1603(3) y = 0.1014(2)	<i>P</i> = 7.5 GPa, room <i>T</i> [8]
α"	Monoclinic	C2/m	a = 5.813(2) b = 3.145(1) c = 5.612(2) $\beta = 113.10(2)^{\circ}$ (x, y, z) = (0.2800(5), 0, 0.2516(6)) c' = 6.300 $\beta' = 55.02^{\circ}$	<i>P</i> = 8.3 GPa, room <i>T</i> [8]
3	Body-centerd tetragonal (bct)	I4/mmm	a = 2.92 b = 4.84	P = 17.5 GPa, room $T[17]$

#### Table 1. Crystal structures of cerium allotropes.

#### Table 2. Nearest bond lengths in cerium phases.

Phase	Bond lengths (Ce-Ce), Å	Volume per Ce, $Å^3$	Lattice parameters, Å	Conditions
α	3.411	28.065	<i>a</i> = 4.824	P = 0.81 GPa, room $T$
β	3.681(6), 3.647(6)	34.784	a = 3.6810 c = 11.857	P = 0, room $T$
γ	3.649	34.367	a = 5.1610	P = 0, room $T$
δ	3.559	34.713	<i>a</i> = 4.11	P = 0, T = 1041  K
α′	2.8435(2), 3.0394(4), 3.0143(2), 3.3098(4)	22.918	a = 3.0143(2) b = 5.8935(3) c = 5.1603(3)	P = 7.5 GPa, room $T$
α″	2.9633(1), 3.1142(2), 3.145(2), 3.3046(4), 3.3525(2), 3.3629(1)	23.593	a = 5.813(2) b = 3.145(1) c = 5.612(2) $\beta = 113.10(2)^{\circ}$	P = 8.3 GPa, room $T$
3	2.92(4), 3.181(4)	20.634	a = 2.92 b = 4.84	P = 12 GPa, room $T$

addition, the liquid phase of cerium is stable in an unusually wide range of temperatures (2648 K), inferior only to thorium. It is believed that plutonium, which also exhibits several allotropies— $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ,  $\delta'$ , ( $\zeta$ )—is the actinide analog of cerium [11].

Among the phase transformations of cerium, the bestknown transition is from  $\gamma$ -Ce to  $\alpha$ -Ce [2]. It is usually observed at room temperature under the pressure  $P \approx 0.8$  GPa, but it can also be induced by decreasing the temperature at atmospheric pressure. In the latter case, the transition goes through the intermediate  $\beta$ -phase [3], which is practically impossible to eliminate afterwards. The  $\gamma \rightarrow \alpha$ transformation was first observed by Bridgman in 1927 [12]. However, the most famous property of the transition—its isostructureness — was established in X-ray experiments only in 1949 and 1950, first by applying pressure [13] and then by decreasing temperature [14]. In both cases, the same facecentered structure for  $\gamma$ -Ce and  $\alpha$ -Ce was reported. The two phases therefore differ only by the numerical value of the fcc lattice constant (see Table 1). Because two energy minima of the same structure had not been observed previously, the issue was considered of great scientific interest. Later, however, other isostructural phase transitions were found, for example, in NpO<sub>2</sub> ( $T_c = 25.5$  K) [19, 18] and YbInCu<sub>4</sub> ( $T_c = 42$  K) [20] (NpO<sub>2</sub> is discussed below in Section 6.6.1). The  $\gamma \rightarrow \alpha$ transition is accompanied by such a big volume change at room temperature (15%) that the term 'volume collapse' was applied to this case (Fig. 2). This volume change is sometimes



**Figure 1.** Pressure–temperature phase diagram of cerium. Interphase  $\alpha$ - $\beta$ - $\gamma$  boundaries are taken from Ref. [2],  $\alpha$ - $\alpha'$ - $\alpha''$  boundaries (corresponding to the directions  $\alpha \rightarrow \alpha'$ ,  $\alpha \rightarrow \alpha''$ , and  $\alpha'' \rightarrow \alpha'$ ) from Ref. [25], the boundary between  $\alpha$  and  $\varepsilon$  phases from Ref. [26], and the refined critical point of the  $\gamma \rightarrow \alpha$  transition is from Ref. [70]. The region of phase ambiguity corresponds to the mixture of phases ( $\alpha$ ,  $\alpha'$ ,  $\alpha''$ , and  $\varepsilon$ ), with the percentage depending on the P-T trajectory leading to a P-T point [25].



Figure 2. Volume change (per cerium atom) at the  $\gamma \rightarrow \alpha$  phase transition under pressure at room temperature. Experimental data are from Ref. [27].

called unique, but this is an overstatement. For example, in passing from graphite to diamond, the volume decrease per carbon atom is much larger (57–69%). In that case, we are dealing with *different covalent bonding* of carbon, which is studied well both theoretically and experimentally. Inspired by the carbon case, we may suggest that in  $\gamma$ -Ce and  $\alpha$ -Ce, we are dealing with *different manifestations of the metallic bond* of cerium. In particular, the metallic bond in  $\gamma$ -Ce can differ from the bond in  $\alpha$ -Ce by its spatial orientation. In that case, the  $\gamma \rightarrow \alpha$  transition would be not a truly isostructural but a hidden structural transition, closely connected with the symmetry change of the cerium electron density. This idea leads to the theory of quadrupolar ordering, which is discussed in Section 6.

In addition to the  $\gamma \rightarrow \alpha$  phase transition, a great scientific discussion was prompted by the problem of the identification of the phase in which cerium transforms from  $\alpha$ -Ce under pressure [8]. As possible candidates, the monoclinic structure (I2/m [10] or C2/m [7, 8]) or base-centered orthorhombic (the  $\alpha$ -U structure) [5,6] were considered. Nowadays, it is established that the symmetry of this phase depends on the method of production and sample history [8]. If a sample is prepared with cold (low-temperature) synthesis, it is transformed into the  $\alpha''$  phase of cerium, which is the monoclinic C2/m structure. If the sample is prepared at a high temperature (and pressure) and cooled to room temperature, the transition is from the  $\alpha$ -cerium to the  $\alpha'$  phase with

the  $\alpha$ -U structure. This question is discussed in general terms in Section 9.

The phase diagram of cerium (Fig. 1) is also constantly discussed and refined, especially in the region of phases  $\alpha$ ,  $\alpha'$ ,  $\alpha''$ , and  $\varepsilon$ , and transitions between them [21–26]. Phase boundaries between them were determined by measuring the electric resistivity of a sample at several P-T points. In the first study [21], the phase boundary between the  $\alpha'$  (or  $\alpha''$ ) and ε phases was found to form a straight line that extrapolated to the minimum of the cerium melting curve. These data were used in reference book [22]. However, already in 1981, a dome-shaped curve of phase boundaries was found in [23], which was later confirmed in [24] and [25]. In [25, 26], the cerium phase diagram was studied in the region of high temperatures and pressures. There, the direct phase transition from the tetragonal phase ( $\epsilon$ ) to the cubic  $\alpha$  phase [25] and the transition in the opposite direction (i.e.,  $\alpha \rightarrow \epsilon$ ) were found at pressures of 7.1 GPa ( $T \approx 735$  K) and 7.2 GPa  $(T \approx 800 \text{ K})$  [24, 26] (see Fig. 1). Based on these studies, a suggestion about the existence of an  $\alpha - \alpha' - \varepsilon$  triple point at 6.9 GPa and 600 was made [26].

In this paper, we consider the abovementioned problems and, in particular, discuss recent experimental data on the  $\gamma \rightarrow \alpha$  phase transition [27–29]. We also review other phase transitions under pressure, paying much attention to theoretical and computational methods.

# 2. Peculiarities of the electronic structure of atomic cerium and the chemical bond of the cerium dimer ( $Ce_2$ )

It is widely accepted that the phase variety of cerium with four valence electrons  $(4f5 6s^2)$  is caused by its single 4f electron. Indeed, cerium is virtually the first element in the periodic table in which an appreciable occupation of the 4f electron shell is realized. However, the direct participation of the 4f states in metal bonding is doubtful. In cerium, the properties of valence electrons, that is, the 4f electron from one side and the 5d6s<sup>2</sup> from the other, are so different that they are grouped into two separate electron subsystems [36]. Three valence 5d6s<sup>2</sup> electrons are usually regarded as conventionally metallic, meaning that they form a typical chemical (metallic) bond, whereas the core-like 4f electron remains mainly localized. This conclusion follows from the radial dependence of the partial electron density (Fig. 3). From the general theory of chemical bonding, it follows that the optimal radius of the cerium atoms is found at the maximal value of its valence electron density. In accordance with this criterion, we see (Fig. 3 and Table 3) that 5d and 6s electrons are actually responsible for the metallic bond, because their electron density is maximal at  $r_{\gamma}$ , which is the contact radius (the radius of touching spheres) of  $\gamma$ -Ce. Meanwhile, the 4f electron does not participate or barely participates in the process, because its average radius  $r_{\rm f}$  is considerably smaller

**Table 3.** Radial maxima  $(\rho(r)r^2)$  of atomic shells and valence electron density of cerium (Å). (The data are obtained from the relativistic atomic calculation of cerium within the density functional theory [107] in the local density approximation [184].) For comparison, the radii  $r_c$  of close contact spheres are  $r_{\gamma} = 1.825$ ,  $r_{\alpha} = 1.706$  in the solid state, and  $r_{Ce_2} = 1.31-1.33$  (Å) in the cerium dimer.

	4f <sub>5/2</sub>	5d <sub>3/2</sub>	$6s_{1/2}$	(5d <sup>1</sup> 6s <sup>2</sup> )	(5d <sup>1.5</sup> 6s <sup>1.5</sup> )	(5d <sup>2</sup> 6s <sup>1</sup> )
<i>r</i> <sub>max</sub>	0.375	1.154	1.971	1.800	1.634	1.379



**Figure 3.** Partial electron density (4f, 5d, 6s<sup>2</sup>) and valence electron density (5d6s<sup>2</sup>) in cerium (the relativistic DFT–LDA calculation of the cerium atom [184]). The radii  $r_{\gamma}$ ,  $r_{\alpha}$ , and  $r_{Ce_2}$  are those of the contact spheres in the  $\gamma$ -phase,  $\alpha$ -phase, and cerium dimer (Ce<sub>2</sub>).

than the characteristic bonding length,  $r_f \ll r_\gamma$  (see Table 3). We see in what follows that this scenario is fully supported by many-electron relativistic calculations of the cerium dimer (Ce<sub>2</sub>) [32, 33].

However, the 4f electron does affect the metallic bonding indirectly, and it certainly cannot be considered an ordinary core electron, which simply screens the nuclear charge. Unlike other core electrons, the 4f shell is open. This fundamental property implies 4f electron degrees of freedom, which are absent in the case of a fully occupied electron shell. The completely filled electron shell leads to a spherically symmetric electron density and to a trivial spherically symmetric potential that screens the nuclear field. In atomic cerium, because of the orbital degrees of freedom, 4f states are grouped (coupled) with states of other valence electrons, 5d and 6s to minimize the resultant intrasite 4f–5d and 4f–6s Coulomb repulsions (Fig. 4 and Table 4). Thus, already in atomic cerium, rather strong 4f–5d and 4f–6s interactions exist that induce 4f–5d [37] and 4f–6s [38] correlations.

These correlations can be found in the atomic spectrum of cerium (see Table 4). Its four valence electrons, 4f5d6s<sup>2</sup>, are grouped into the <sup>1</sup>G<sub>4</sub> many-electron ground state with the spin quantum number S = 0, whereas according to the first Hund rule, S should be maximal [40]. In atomic physics, this is a rare case of the first Hund rule *violation* [40]. The origin of the anomaly is discussed in detail in Ref. [39], where it is shown that in the <sup>1</sup>G<sub>4</sub> state, the quartic Fermi hole of the



**Figure 4.** Main electronic interactions between two neighboring cerium atoms in a crystal: (a) intra-atomic Coulomb repulsion ('Hund-rule coupling'), (b) chemical (metallic) bond between overlapping d- and s-electrons, (c) intersite Coulomb 4f-4f interaction. Because the last interaction is the weakest, it is responsible for the low-lying excitations.

fourth order is formed that optimizes the energy of the 4f–5d Coulomb repulsion.

To describe cerium in the condensed state, the authors of Refs [41–43] model many-electron effects of the  $4f5d6s^2$  valence shell by introducing a spin polarization and an orbital term, which artificially restore the first Hund rule for atoms of Ce. Taking into account that the first Hund rule is not valid for the  ${}^{1}G_{4}$  ground state of the cerium atom, the correctness of the approach and its results are under question.

Another peculiarity is the presence of the excited 4f5d<sup>2</sup>6s configuration (see <sup>5</sup>H in Table 4), which dominates in the cerium atomic spectrum starting from 0.29 eV. Clearly, 4f5d<sup>2</sup>6s mixes with 4f5d6s<sup>2</sup> in molecules and solids. Indeed, the 6s  $\rightarrow$  5d transition can potentially lead to a strengthening of chemical bonding because the 6s shell becomes unoccupied and allows the formation of a 6s-6s bonding between neighboring cerium atoms in molecules and solids. As shown in Table 3 and Fig. 3, the strengthening of metallic bonding results in an effective decrease in the characteristic radii and bond lengths. Interestingly, a partial increase in the d-orbital occupation was found in the Compton scattering experiment [44], and hence the discussed transfer indeed occurs at the  $\gamma \rightarrow \alpha$  phase transition in cerium. It is worth noting that based on the effective unit cell energy, it was concluded that various solid phases differ from each other not only by crystal structure but also by their electronic structure [46]. Different electronic structures of  $\gamma$  and  $\alpha$  cerium were also found in optical conductivity measurements [47].

It is instructive to study the peculiarities of chemical bond formation in the cerium dimer [34], because it is the simplest electron system and the simplest molecular bond binding two cerium atoms. Here, many-electron calculations are to be done where relativistic effects are taken into account. Calculations of that level have become possible only recently [32, 33]. According to their results, a triple bond is realized in Ce<sub>2</sub>: the first bond is formed between 6s states of neighboring atoms, two others are between 5d states. [If two cerium nuclei lie on the z axis, the double d-bond is formed between the dfunctions of two cerium atoms with the same azimuthal dependence (m), that is, between exp  $(-\varphi i)$  and exp  $(-\varphi i)$ ,

Leading configuration	Term	J	g (Lande)	$\Delta E$ , eV, experiment [45]	$\Delta E$ , eV [33]
4f5d6s <sup>2</sup>	$^{1}G$	4	0.945	0	0
4f5d6s <sup>2</sup>	<sup>3</sup> F	2	0.765	0.028	0.076
		3	1.077	0.206	0.197
		4	1.077	0.384	0.397
4f5d6s <sup>2</sup>	<sup>3</sup> H	4	0.890	0.159	0.188
		5	1.032	0.274	0.305
		6	1.160	0.493	0.539
4f5d6s <sup>2</sup>	<sup>3</sup> G	3	0.735	0.172	0.227
		5	1.150	0.521	0.521
4f5d <sup>2</sup> 6s	<sup>5</sup> H	3	0.600	0.294	0.299
		4	0.986	0.302	0.340
		6	1.166	0.589	0.631
		7	1.237	0.719	0.752
4f5d6s <sup>2</sup>	<sup>1</sup> D	2	0.937	0.295	0.338
4f5d <sup>2</sup> 6s	<sup>5</sup> I	4	0.666	0.396	0.602
		5	0.907	0.467	0.690
		6	1.117	0.552	0.797
		7	1.216	0.659	0.921
		8	1.250	0.844	1.066
$4f^{2}6s^{2}$	<sup>3</sup> H	4	0.805	0.591	
		5	1.035	0.774	
		6	1.169	0.965	

Table 4. Low-lying energy spectrum of the cerium atom.

and between  $\exp(+\varphi i)$  and  $\exp(+\varphi i)$ .] Correspondingly, there are six valence electrons on this bond:  $(6s\sigma_g)^2(5d\pi_u)^4$ (the  ${}^{1}\Sigma_{g}^{+}$  many-electron state). More importantly, one 4f electron remains in each cerium atom that does not participate in chemical bonding. The conclusion on the inertness of 4f states is nontrivial. For example, in the uranium dimer (U<sub>2</sub>), 5f states behave differently and do participate in the formation of a quintuple chemical bond [48].

Although the two remaining 4f electrons of cerium do not form a chemical bond, they play an important role in the lowlying excitation spectrum of Ce2. In ab initio calculations [32, 33], six low-lying many-electron states  $({}^{1}\Sigma_{g}^{+}, {}^{1}\Sigma_{u}^{-}, {}^{3}\Sigma_{g}^{-}, {}^{3}\Sigma_{u}^{+}, {}^{3}6_{u}, {}^{1}6_{g})$  were found that are practically indistinguishable (0.01–0.07 eV). In [49], it is shown that the existence of such excitations is caused by 4f-4f interactions, where the dominant one is the Coulomb repulsion of two localized 4f electrons. Hence, the following scenario is realized in cerium (Fig. 4). The chemical bond of  $Ce_2$  is made of 5d and 6s electron states that form occupied molecular orbitals. The fixed bonding 5d and 6s orbitals directly influence the space of 4f states via Coulomb repulsion. The effective active space of the 4f states is narrowed to just two orbital f-states [with the azimuthal dependences  $\exp(-3\varphi i)$  and  $\exp(+3\varphi i)$ ]. But unlike in other valence states (5d and 6s), the electron degrees of freedom of the localized f-electron are still not completely frozen. These electron degrees of freedom of nearly degenerate 4f states are responsible for the low-lying molecular energy spectrum. It is conceivable that the same scenario is realized in crystalline cerium.

# 3. $\gamma \rightarrow \alpha$ phase transition in cerium (review of models)

As noted in the Introduction, the unusual feature of the  $\gamma \rightarrow \alpha$  phase transition is its isostructural nature, discovered

in 1949–1950 [13, 14]. In 1970–1980, the focus was on different magnetic properties of the  $\gamma$  and  $\alpha$  phases [2, 50–52], and theoretical models were expected to explain this difference.

The magnetic susceptibility  $\chi_{\gamma}$  of  $\gamma$ -cerium follows the Curie–Weiss law ( $\Theta = -50$  or -9 K,  $p_{eff} = (2.4 - 2.52) \mu_B$ ) [50, 51] with an effective magnetic moment close to the value  $p_{\rm eff} = 2.54 \mu_{\rm B}$  for a single free f-electron. The magnetic susceptibility of  $\alpha$ -cerium shows only a weak dependence on temperature, and therefore  $\alpha$ -Ce is characterized as a Pauli paramagnet [52, 53]. However, the minimal value of  $\chi_{\alpha}$  (at  $T \approx 50$  K) is 4.5 times larger than the value deduced from electronic specific heat measurements [53]. The susceptibility  $\chi_{\alpha}$  demonstrates a slow increase with temperature for T > 60 K and a steep increase on decreasing the temperature to T < 20 K (which is usually accounted for by  $\beta$ -impurities). The data are conventionally explained by the presence of nearly free f-electrons in the  $\gamma$  phase, which become bound in the  $\alpha$  phase. But this is a simplistic interpretation. Indeed, we saw in Section 2 that the f-electron is not free even in the cerium atom, because it interacts with d- and s-valence electrons via Coulomb repulsion. The strength of this interaction is of the order of 1 eV (see Table 4), and hence the fact that the effective magnetic moment coincides with that of a free f-electron is probably coincidental [49]. In condensed cerium, as in the dimer, there can be low-lying many-electron 4f excitations. These excitations can be magnetic (with a nonzero magnetic moment) or nonmagnetic (with a zero magnetic moment). Their characteristic splittings are of the order of 10-100 K, and currently it is practically impossible to predict their energy positions with confidence. (Nevertheless, this can be done in some cases; see Ref. [49].)

The  $\gamma \rightarrow \alpha$  transition is possibly a record holder for the number of models suggested for its description. First, it was

considered that the localized f-electron that is present in the  $\gamma$  phase becomes part of the metallic (6s5d) band in the  $\alpha$  phase. This is the promotional model [54–56], which at that time was linked with the cerium valence instability [57, 58]. According to this model, the transition occurs as

$$(\gamma$$
-Ce) 4f<sup>1</sup>5d<sup>1</sup>6s<sup>2</sup>  $\rightarrow$  4f<sup>0</sup>5d<sup>2</sup>6s<sup>2</sup>( $\alpha$ -Ce),

whence it follows that the  $\gamma$  and  $\alpha$  phases differ by the number of f-electrons. This conclusion was checked in positron annihilation experiments [59, 60] and in Compton scattering experiments [44]. In both cases, nearly equal occupation of the f-states  $(n_f \approx 1)$  was established, and the promotional mechanism was concluded to be irrelevant. This fact is supported by an accurate theoretical consideration. Indeed, the  $4f \rightarrow 5d \ (4f \rightarrow 6s)$  transition is very energy consuming. The required energy can be approximated by 4 eV from the experimentally measured transitions  $(4f5d^2(4H_{7/2}) \rightarrow 5d^3 \text{ in})$  $Ce^{1+}$  [45]). In addition, the calculations of the electron band structure of the  $\gamma$  and  $\alpha$  phases by the density functional theory (DFT) in the local density approximation (LDA) have shown that the number of occupied f-states in both phases is almost equal to one per cerium atom [61]. Recently, the conclusion concerning the number and nature of f-states was even strengthened: inelastic neutron scattering experiments indicate that the 4f electron remains localized at the  $\gamma \rightarrow \alpha$  phase transition [62, 63].

A detailed analysis on the partial occupations of valence states in the  $\gamma$  and  $\alpha$  phases given in the Compton scattering measurements [44] is particularly worth mentioning. It has turned out that the number of 4f electrons in the  $\alpha$  phase is close to one, and even a small change in the occupation number leads to a worsening of the correspondence between the experiment and the model. At the same time, the occupation numbers of d- and s-states do change: in the  $\alpha$  phase, the number of d-states increases by 0.6, which perfectly fits the scenario of the chemical bonding discussed in Section 2.

In 1974, having analyzed the thermodynamic properties of cerium, Johansson put forward a Mott-like (localization– delocalization) model for the 4f-electron subsystem at the  $\gamma \rightarrow \alpha$  phase transformation [36]. Now the number of 4f electrons remains constant in both phases, but the change concerns their nature: in the  $\alpha$  phase, the electrons are bandlike, while in the  $\gamma$  phase, they are localized. Two fcc phases ( $\gamma$  and  $\alpha$ ) then correspond to two minima of the free energy, which develop within the same space symmetry ( $Fm\bar{3}m$ ). Later, the theory was confirmed by model band structure calculations of cerium [41–43, 64].

The description of the  $\gamma \rightarrow \alpha$  transition in cerium and other metals (for example, in actinides [65, 66]) within the dilemma of localization-delocalization of f-states [36, 41–43, 64] has become widespread. However, the explanation of the physical and chemical properties within the concept remains essentially one-electronic. In the many-electron approach, this contradistinction is not really relevant. Indeed, the localized atomic or the delocalized Bloch functions are only characteristics of different basic sets. From the Bloch states, by a corresponding linear transformation, we can obtain the localized atomic functions and vice versa, whereas the correct solution to the electronic problem should not depend on the choice of the basis set. One can say, of course, that the Bloch functions are preferable because they explicitly take the translation symmetry of a crystal into account. But the Bloch functions are symmetry adapted only for the one-electron problem. In the realistic many-electron case, the translation symmetry is exact only if all crystal electrons are subjected to a translation. The situation here is completely analogous to the many-electron atomic one. In the atomic problem, the manyelectron Hamiltonian is invariant under rotations that act on all electrons of the atom. In the case of only one-electron rotation, the Hamiltonian is not invariant. The same holds for crystal translations in the many-electron case.

There is another approach, called the Kondo volume collapse model, which competes with the theory of a Mottlike transition in cerium [30, 31, 67]. From its name, it is clear that the model exploits a large volume change at the transition and the Kondo mechanism [68] for demagnetization of magnetic moments. In the Kondo model, the 4f electron in the first approximation stays localized in the  $\gamma$  and  $\alpha$  phases, but the interaction between the 4f electrons and band electrons at the Fermi level is much more intense in the  $\alpha$ phase. Quantitatively, this implies that the Kondo temperature is small (50–100 K) in the  $\gamma$  phase and is relatively large (1000–2000 K) in the  $\alpha$  phase. In addition, the so-called hybridization between 4f and band states gives rise to the formation of a singlet ground state, which is separated from the magnetic states by an energy gap of  $k_{\rm B}T_{\rm K}$ . Hence, the last feature to be explained is the appearance of two minima of the same fcc lattice. It is worth noting that such behavior has not been observed in molecular structures. Molecules often have close energy minima, but these always correspond to different structures (conformations). Therefore, in order to describe two minima, the Kondo model always exploits a nonlinear empirical dependence. In the first formulation, that was the dependence of the Kondo temperature on the cerium unit cell volume [30]. In the recent formulation, the dependence of an effective Debye temperature is used [70].

Another shortcoming of the model (as well as of the model of localization–delocalization of the 4f-electron density) is that it is effective only for one unique phase transition  $(\gamma \rightarrow \alpha)$ . The other phase changes in cerium should then be explained by traditional means. One phase transition  $(\gamma \rightarrow \alpha)$  is thus singled out from the whole set of phase transformations, which is not completely logical.

Two abovementioned models (Mott-like and Kondo-like for 4f states) have been actively developed over the last 20 years, and have become more and more complicated from the technical standpoint (see Section 5.1). Nowadays, the Kondo effect is described within the dynamical mean-field theory (DMFT) (see Section 5.2) and has lost the characteristics of an empirical approach. But even today, there is no consensus on the ultimate approval of just one of these models [70 71]. We finally note that recent inelastic neutron scattering measurements of  $\alpha$ -Ce (in a sample doped by 10 at.% Sc) [62] have found that its magnetic form factor differs appreciably from the one calculated in [42], where the 4f states are considered itinerant (delocalized) (Fig. 5). According to Ref. [62], the 4f electrons remain localized even in  $\alpha$ -Ce. This conclusion is in full agreement with papers [32, 33] on the many-electron calculations of the cerium dimer, from which it also follows that the 4f electrons do not participate in chemical bonding (see Section 2). It is worth mentioning that in both the Kondo model and the localization-delocalization model of the 4f electron subsystem, the isostructural nature of the phase transition has never been questioned and has always been considered a well-established fact. However, there is another approach [73-75], which



**Figure 5.** The magnetic form factor  $F^2(Q)$  in  $\alpha$ -Ce (in Ce<sub>0.9</sub>Sc<sub>0.1</sub>) obtained by high-energy neutron inelastic scattering measurements [62]. The solid curve through the experimental data corresponds to the Ce<sup>3+</sup> form factor [72]. The dotted line is a calculated theoretical curve for the itinerant 4f electrons (LMTO–LDA method) [42].

treats the phase change as a *hidden structural* transformation (see Section 6). In 2010, this approach for the first time received experimental support [28, 29]. There also appeared experimental evidence of the active role of the lattice in the  $\gamma \rightarrow \alpha$  transition [27].

# 4. Significant role of the lattice in the $\gamma \rightarrow \alpha$ transition

Until the work of Jeong et al. [27], it was assumed that the cerium lattice plays a passive role in the  $\gamma \rightarrow \alpha$  transition, often disregarded in theoretical models. In [27], it was first emphasized that the vibrational contribution to the entropy change per atom  $(\Delta S_{\rm vib}^{\gamma-\alpha} \approx (0.75 \pm 0.15) k_{\rm B})$ , where  $k_{\rm B}$  is the Boltzmann constant) is about half the total entropy change (1.5 $k_{\rm B}$  [2]). In this section, we consider the active role of the lattice in the  $\gamma \rightarrow \alpha$  transition, which manifests itself through a softening of some phonon branches of  $\gamma$ -cerium [76, 77] and a softening of the bulk modulus [78, 79], which eventually results in such a large lattice contribution to the transition entropy change [27, 80].

### 4.1 Softening of the bulk modulus at the $\gamma \to \alpha$ transition and other elastic phenomena

Elastic phenomena in the  $\gamma \rightarrow \alpha$  transition were first observed and reported in [78]. At room temperature in polycrystalline cerium, the authors monitored the bulk modulus B, the shear modulus  $G = c_{44}$ , the effective Debye temperature  $\Theta_D$ , and the Poisson ratio as functions of the applied pressure in ultrasound measurements. As the pressure increased above 0.4 GPa and approached the onset of the  $\gamma \rightarrow \alpha$  transition, they found that the Poisson ratio fast decreased while G slowly increased and the Debye temperature  $\Theta_{\rm D}$  remained nearly constant. Upon completing the transition to the  $\alpha$  phase, all elastic moduli and the Debye temperature increased stepwise, after which they continued to rise slowly. This behavior was further confirmed in more precise measurements [69, 79]. In [79], experimental data were collected up to the pressure of 9 GPa, thus covering not only the  $\gamma \rightarrow \alpha$  but also the next  $\alpha \rightarrow \alpha'$  (or  $\alpha \rightarrow \alpha''$  [8]) phase transition.

The phonon frequencies of  $\gamma$ -cerium single crystals along the [100], [110], [111], and [0 $\xi$ 1] high-symmetry directions of the Brillouin zone were studied in [76, 77] (Fig. 6). The



**Figure 6.** Phonon dispersion curves of  $\gamma$ -Ce (295 K) extracted from inelastic neutron scattering measurements [76]. The solid lines were obtained by fitting the data in the force constant model (the Born–von Kárman model with 8 nearest coordination shells).

comparison of the phonon dispersion curves with those of thorium [81] shows that the spectrum of  $\gamma$ -cerium is in general softer (i.e., its vibration frequencies are smaller) than can be expected from the Lindemann criterion for melting. The softening is more pronounced for the longitudinal (L) modes and the T [111] and T<sub>1</sub>[110] transverse modes, and less pronounced for the T<sub>2</sub>[110] and T [100] branches (see Fig. 6). The T [100] mode almost corresponds to that of thorium (no softening) [81]. Therefore, the softening is absent for those branches (T [100] and T<sub>2</sub> [100]) that have no connection with the elastic constants  $c_{11}$  and  $c_{12}$  in the long-wavelength limit ( $\mathbf{q} \rightarrow 0$ ). The dominant effect—softening of the phonon spectrum of  $\gamma$ -Ce—is directly related to the decrease in its bulk modulus  $B = (c_{11} + 2c_{12})/3$ .

We note that the very low frequencies along the  $\Gamma - L$  line (the T [111] curve) are caused by another (martensitic) phase transition,  $\gamma \rightarrow \beta$  (fcc  $\rightarrow$  dhcp), which occurs at 260 K (see Section 8). This conclusion is supported by the anomalous behavior of phonon modes around the L point  $(2\pi/a)$  (1/2, 1/2, 1/2) of the Brillouin zone [77]. The frequency at the L point decreases as the temperature decreases from 0.94 Hz (875 K) to 0.82 THz (295 K), while the reverse effect is observed for the other modes of  $\gamma$ -cerium [77]. The same soft mode ( $\approx 0.82$  THz) at the L point was also found in lanthanum (T = 660 K), where a transition of the same type occurs: fcc  $\rightarrow$  dhcp. (The fcc  $\rightarrow$  dhcp transformation involves four transverse waves propagating along the [111] direction with three reduced vectors  $(2\pi/a)(\xi, \xi, \xi)$ , where  $\xi = 1/4$  and 1/2 [82].)

From the dispersal curves of  $\gamma$ -cerium, the authors of [76, 77] found the atomic force constants of the Bornvon Kárman model (Table 5), which fully determine the phonon spectrum, that is, the effective Debye temperature  $\Theta_{\rm D}(T)$  ( $\Theta_{\rm D} = 119 - 135$  K) and the elastic constants  $c_{11} = 2.41$ ,  $c_{12} = 1.02$ , and  $c_{44} = 1.94$  in  $10^{10}$  N m<sup>-2</sup> or  $10^{11}$  dynes cm<sup>-2</sup>. Also, they concluded that there was no well-defined low-energy crystal field excitation in  $\gamma$ -Ce. The obtained values of the elastic constants imply a large crystal anisotropy. In particular, the shear elastic constant  $c_{44}$  is three times larger than the quantity

$$c' = \frac{c_{11} - c_{12}}{2} \,, \tag{1}$$

$\mathbf{R}_n$	Ν	xx	уу	ZZ	xy	XZ	yz	
a(1/2, 1/2, 0)	12	4.373		-0.226	4.580			
a(1, 0, 0)	6	-2.356	0.077					
a(1, 1/2, 1/2)	24	0.206	0.317			-0.050	-0.055	
a(1, 1, 0)	12	0.123		0.011	0.151			
a(3/2, 1/2, 0)	24	-0.053	-0.099	-0.104	0.019			
a(1, 1, 1)	8	-0.332					-0.219	
a(3/2, 1, 1/2)	48	0.106	-0.114	0.026	-0.007	0.076	0.005	
a(2,0,0)	6	0.001	0.222					

**Table 5.** Force constants  $\Phi_{\alpha\beta}(\mathbf{R}_n)$  (in n m<sup>-1</sup> or 10<sup>3</sup> dynes cm<sup>-1</sup>) of  $\gamma$ -Ce in the Born–von Kárman model with 8 nearest coordination shells obtained by fitting the phonon spectrum [76]. *N* is the number of atoms in the shell,  $\alpha(\beta) = x, y, z$ .

that is,  $A = c_{44}/c' = 2.8$ . It has turned out that the anisotropy is even higher in the high-temperature  $\delta$  phase (bcc): A = 5.6[82]. The phonon spectrum of  $\delta$ -Ce [82] and its peculiarities are discussed in detail in Section 8.

The dependence of phonon dispersion on pressure at room temperature was recently studied by high-energyresolution inelastic X-ray scattering [80]. Notably, the phonon dispersion curves of  $\alpha$ -Ce were obtained in this work for the first time at P = 0.8 and 2.5 GPa. The dispersion curves were found to change mainly along the [110] and [111] directions, with the most noticeable difference in the vicinity of the X point. The Gruneisen parameters  $\gamma \rightarrow \alpha$  for the T [001], T<sub>2</sub>[110], and L[110] modes become negative around the X point, which on the one hand implies a phase instability and on the other points to its special role.

The behavior of the bulk modulus in polycrystalline cerium samples in the proximity of the  $\gamma \rightarrow \alpha$  transition was studied in [27], by finite differences of the P-V data,  $B = -V dP/dV \approx -V\Delta P/\Delta V$  (Fig. 7). Pronounced softening of the bulk modulus of the  $\gamma$  phase as the pressure approaches the onset of the phase transition is an indication of an increasing elastic instability of the lattice, and the discontinuity of  $B_T$  at the transition implies that the transition is of the first order. The bulk modulus in the  $\gamma$  phase can be fitted by a polynomial dependence  $B_T \propto |P-P_c|^{\alpha}$  ( $P_c = 0.83$  GPa,  $\alpha = 0.46$ ). The obtained isothermal bulk modulus  $B_T$  is in good agreement with the adiabatic bulk modulus  $B_S$  obtained



**Figure 7.** Bulk modulus vs pressure at the  $\gamma \rightarrow \alpha$  transition; the figure and data are from Ref. [27]. Insert: the dotted line is a result of fitting in the range  $0.7 \leq P \leq 0.83$  GPa according to the formula  $B_T \propto |P - P_c|^{\alpha}$ , where  $P_c = 0.83$  GPa and  $\alpha = 0.46$ . The dashed line in the  $\alpha$  phase is taken from Ref. [183].

from ultrasound measurements in [78, 79]. In the cubic phase, the bulk modulus is given as

$$B = \frac{1}{3} \left( 3c_{11} - 4c' + P \right),$$

where c' is the shear modulus and *P* is the applied hydrostatic pressure. In a first approximation, c' is independent of pressure [78, 79, 69], and therefore the softening of the bulk modulus is directly related to the softening of  $c_{11}$ . This conclusion is confirmed by the softening of the measured longitudinal sound velocity with increasing pressure [78, 79, 69] and the transverse phonon frequencies at normal pressure [76].

### **4.2** Atomic mean square displacements and the lattice contribution to the entropy change

In Refs [27, 83], a new experimental technique [27] was used to study isotropic mean square thermal displacements of atoms in  $\gamma$ -Ce and  $\alpha$ -Ce. Traditionally, phonon spectra are obtained from inelastic neutron scattering or from highenergy-resolution inelastic X-ray scattering, often obtained in synchrotron radiation measurements. In both cases, a single crystal is required, whereas powder samples are considered inappropriate for the purpose. However, the study of the  $\gamma \rightarrow \alpha$  transition in cerium single crystal involves some serious technical problems (see Section 7). Therefore, the alternative approach based on the analysis of the atomic pair distribution function obtained by means of high-energy synchrotron and pulsed neutron sources in powder samples is of great importance [84]. The pair distribution function is a real-space Fourier transform of the diffraction spectrum. From the pair distribution function (the peak positions and widths), we can obtain the mean square thermal displacements of cerium nuclei  $\langle u_{iso}^2 \rangle$ , which are then used for further analysis. In Ref. [27], the mean square thermal displacement  $\langle u_{iso}^2 \rangle$  of a cerium atom in the crystal lattice in  $\gamma$  and  $\alpha$  phases was studied as a function of temperature at 0.412 and 0.527 GPa and a function of pressure at 300 K. In the Debye approximation, this quantity is given by

$$\langle u^2 \rangle = \langle u^2 \rangle_0 + \frac{3\hbar}{M\omega_{\rm D}} \left[ \frac{1}{4} + \left( \frac{T}{\Theta_{\rm D}} \right)^2 \Phi_1 \right],$$

where  $\Theta_{\rm D} = \hbar \omega_{\rm D} / k_{\rm B}$  is the Debye temperature,  $\langle u^2 \rangle_0$  is a temperature-independent constant, and

$$\Phi_{1} = \int_{0}^{\Theta_{D}/T} x (\exp(x) - 1)^{-1} dx.$$

By linear fitting, the authors of Ref. [27] extracted the Debye temperatures for both phases:  $\Theta_{\rm D}^{\gamma} = 104(3)$  K and  $\Theta_{\rm D}^{\alpha} = 133(3)$  K.

At high temperatures  $(T > \Theta_D)$ , the vibrational contribution to the entropy change is given by

$$\Delta S_{\mathrm{vib}} \approx 3Nk_{\mathrm{B}} \left[ 1 + \ln \frac{T}{\Theta_0} + \dots \right],$$

where  $\Theta_0$  is the logarithmic phonon moment (it is assumed that  $\Theta_0 = \Theta_D$  in what follows). We then obtain

$$\Delta S_{\rm vib}^{\gamma-\alpha} \equiv \Delta S_{\rm vib}^{\gamma} - \Delta S_{\rm vib}^{\alpha} \approx 3k_{\rm B} \ln \frac{\Theta_{\rm D}^{\alpha}}{\Theta_{\rm D}^{\gamma}}$$

From the last expression, it follows that

$$\Delta S_{\rm vib}^{\gamma-\alpha} \approx 3k_{\rm B} \, \ln \frac{133(\pm 3)}{104(\pm 3)} = (0.75 \pm 0.15) \, k_{\rm B} \, .$$

Thus, according to [27], the estimated vibrational entropy change per atom in the  $\gamma \rightarrow \alpha$  transition,  $\Delta S_{\text{vib}}^{\gamma-\alpha}$ , is about half the total entropy change  $\Delta S_{\text{tot}}^{\gamma-\alpha} = 1.5k_{\text{B}}$  obtained from the latent heat and the Clausius–Clapeyron relation [2]

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta S_{\mathrm{tot}}^{\gamma-\alpha}}{\Delta V^{\gamma-\alpha}} \; .$$

The phonon dispersion of cerium as a function of pressure was recently studied by high-energy-resolution inelastic X-ray scattering [80]. Although the authors have confirmed an appreciable contribution to the  $\gamma - \alpha$  transition entropy, their result  $\Delta S_{\rm vib}^{\gamma - \alpha} = 0.33k_{\rm B}$  differs from the one in [27] quantitatively. For completeness, we quote the Debye temperature and  $\langle u_{\rm iso}^{2} \rangle$  obtained in [80] just before and after the phase transition:  $\Theta_{\rm D}^{\gamma} = 122$  K,  $\Theta_{\rm D}^{\alpha} = 138$  K;  $\langle u_{\rm iso}^{2} \rangle = 0.0206$  Å<sup>2</sup> in  $\gamma$ -Ce and 0.0168 Å in  $\alpha$ -Ce.

#### 4.3 Interpretation of experimental data

It is pointed out in [27] that the dependence of the thermal mean square displacement  $\langle u^2 \rangle$  on temperature or pressure and the behavior of the bulk modulus  $B_T$  in the  $\gamma \rightarrow \alpha$  transition can be described by a well-known model [85, 86], where the energy contribution (of the order-parameter-strain-field coupling type) has the functional form

$$\Delta F_{\rm vib} = \lambda \varepsilon \rho^2 \,. \tag{2}$$

Here,  $\varepsilon$  is a characteristic lattice strain (a component of the strain tensor) and  $\rho$  is the order parameter amplitude. The effect of lattice softening preceding a structural phase transition is a universal feature of coupling (2). The physical mechanism responsible for the elastic instability and a renormalization of the bulk modulus were first studied theoretically in [85, 86]. These models and the form of Eqn (2) itself indicate that the lattice displacements (volume collapse) are secondary parameters. We note that a contribution of exactly the same type has been obtained in the quadrupolar model (see Eqs (6) and (7) below and Sections 6.2, 6.3).

The authors of Ref. [27] also point out an inconsistency with the Kondo volume collapse model, because the estimated value  $\Delta S_{\text{tot}}^{\text{Kondo}} = k_{\text{B}} \ln (2J+1)$ , where J = 5/2, overestimates the experimental value  $\Delta S_{\text{tot}}^{\gamma-\alpha}$  by 15%. Hence, in the Kondo volume collapse model, there is simply no room for the lattice contribution  $\Delta S_{\text{vib}}^{\gamma-\alpha}$ . It is not the first time such inconsistencies have appeared. Earlier, a serious discussion was prompted by the interpretation of resonance photoemission spectra [87, 8].

In recent studies [70] and [89], attempts were made to incorporate the lattice contribution into the Kondo approach and remove the discrepancy in the framework of an empirical Kondo model and the DMFT, correspondingly.

## 5. Models of the electronic structure of $\gamma$ -Ce and $\alpha$ -Ce without space symmetry change

Cerium is a unique element in the theory of the electron structure of correlated metals, with its  $\gamma \rightarrow \alpha$  transition being a testing ground for the implementation of new theoretical approaches in computational solid state physics. This results in a great number of studies in which its electronic structure is modeled [41–43, 64, 65, 71, 90–103], starting with the first DFT–LDA calculation [90] and ending with recent work [96–102] within the DMFT [104, 105]. Some of the studies, along with principal approximations and computed characteristics, are given in Table 6.

It is very important to note that in all these calculations [41–43, 64, 65, 71, 90–103], the isostructural nature of the transition is taken for granted. However, new experimental data that emerged recently indicate that the  $\gamma \rightarrow \alpha$  phase change is a hidden structural transition (see Sections 6 and 7) [28, 29, 73–75, 37].

#### 5.1 Electron band structure calculations of cerium

One of the first calculations of cerium was done by Glötzel [90] within the local spin density approximation of the DFT. In the spin-polarized treatment corresponding to the unrestricted Hartree-Fock method [106], the electron density is split into spin-up and spin-down components, and an empirical expression [107] of the free electron gas is used for the exchange interaction. In this approach, the description of  $\gamma$ -Ce is unsatisfactory, because the ground state is ferromagnetic with a wrong equilibrium volume. Subsequent studies followed the path of more and more sophisticated computational schemes, which incorporated uncontrolled empirical approaches. For example, in [41-43], a so-called orbital polarization was introduced, that is, an energy term was added to the effective one-electron Hamiltonian to simulate three Hund's rules for cerium. This procedure ignores the fact that the first Hund rule is violated in the cerium atom (see Section 2). In [92-95], band structure calculations were corrected to explicitly exclude the selfinteraction of the localized 4f states of cerium. (The electron self-interaction [108] is an artifact of the local density approximation of the DFT, which appears as a result of a mismatch between the exact Coulomb and an approximate exchange interaction.)

Correlation effects caused by the many-electron Coulomb repulsion are conventionally reduced to the Hubbard interaction and a multiplet splitting of the localized 4f levels [109] (the so-called 'Hubbard I' or 'LDA<sup>++</sup>' approximation). It is notable, however, that all correlation effects in that approach are limited to the 4f states. The band (spd) electrons of cerium are treated in the one-electron approximation (as an electron background or so-called 'electron thermostat'). This is a serious approximation by itself. In Ref. [38], it is shown that by averaging the single-site s–f interactions, we retain only

 Ref.	Authors	Year	Main approximations	Calculated characteristics
[90]	Glötzel D	1978	Spin-polarized muffin-tin LMTO (DFT–LDA)	Equilibrium lattice constants, bulk modulus, magnetic susceptibility of $\gamma$ -Ce, La, Th
 [61]	Pickett W E, Freeman A J, Koelling D D	1981	Non-muffin-tin LAPW (DFT–LDA)	Magnetic susceptibility, occupation of 4f states in cerium
[41]	Eriksson O, Brooks M S S, Johansson B	1990	Spin and orbital polarization in LMTO (DFT-LDA), simulation of Hund rules	Equilibrium volumes in $\gamma\text{-Ce}$ and $\alpha\text{-Ce}$
[92]	Svane A	1994	Self-interaction correction for 4f states, spin-polarization in DFT–LDA	Equilibrium volumes in $\gamma\text{-Ce}$ and $\alpha\text{-Ce}$
[93]	Szotek Z, Temmerman WM, Winter H	1994	Self-interaction correction for 4f states, spin-polarization in DFT–LDA	Equilibrium volumes and magnetic moments in $\gamma$ -Ce and $\alpha$ -Ce
 [64]	Johansson B et al.	1995	Mott-like transition in DFT–LDA	$\gamma \rightarrow \alpha$ phase diagram, critical point, free energy contributions
 [91]	Söderlind P et al.	1995	Generalized gradient approximation (GGA), spin-polarization in DFT–LDA, full potential	Equilibrium volume, bulk modulus, equation of state for $\alpha$ -Ce
[95]	Laegsgaard J, Svane A	1999	Self-interaction correction for 4f states, magnetic impurity in DFT-LDA	Equilibrium volumes and magnetic mo- ments in $\gamma$ -Ce and $\alpha$ -Ce, temperature effects
 [96]	Zölfl M B et al.	2001	Dynamic mean-field theory (DMFT) with DFT-LDA	Equilibrium volumes, photoemission spectra of $\gamma$ -Ce and $\alpha$ -Ce, etc.
 [97]	Held K, McMahan A K, Scalettar R T	2001	Dynamic mean-field theory (DMFT) with DFT–LDA, quantum Monte Carlo	Equilibrium volumes and magnetic moments in $\gamma$ -Ce and $\alpha$ -Ce
 [99]	Haule K et al.	2005	Dynamic mean-field theory (DMFT) with DFT-LDA	Optical conductivity for $\gamma$ -Ce and $\alpha$ -Ce and comparison with experiment [47]
 [89]	Amadon B et al.	2006	Dynamic mean-field theory (DMFT) with DFT-LDA for LMTO	Entropy change at the $\gamma \rightarrow \alpha$ transition, equilibrium volumes, photoemission spectra

Table 6. Electronic structure of  $\gamma$ -Ce and  $\alpha$ -Ce in various band structure models.

even terms for cubic crystals, and thus exclude important odd electron density fluctuations that appear in the exchange between s- and f-electrons (octupole interactions in terms of the multipole expansion).

#### 5.2 Dynamic mean-field theory (DMFT)

Over the last decade, methods of the dynamic mean-field theory [104, 105] have been used for describing the peculiarities of the  $\gamma \rightarrow \alpha$  phase transition [96–102]. The DMFT is an approximation to the electronic problem in a crystal lattice when the electron problem with many degrees of freedom is reduced to a single-impurity problem with essentially fewer degrees of freedom. The approximation becomes exact in the hypothetical limit  $z \rightarrow \infty$ , where z is the number of nearest neighbors (in practice,  $z \propto 2-12$ ). The nearest neighbors are thus replaced with a one-electron 'thermostat'. It is believed that the DMFT gives a better description than the Mott-like and K ondo models.

The DMFT accounts for the hybridization between localized f-electron states and also between the delocalized spd- and localized f-electrons. The problem is first solved in an effective one-electron approximation, which gives computed electron bands formed by the spdf states. Then the Coulomb interaction in the form of the Hubbard repulsion  $U \approx 6 \text{ eV}$  is introduced and a certain realization of the DMFT is applied. As a DMFT solver, the noncrossing approximation (NCA) [96] or the quantum Monte Carlo (QMC) method and Hubbard-I approximation [98] can be used. The main finding is that at zero temperature, the energy minimum corresponds to  $\alpha$ -Ce, but as the temperature is increased to 0.14 eV, the minimum is shifted to a larger volume, which is interpreted as the  $\gamma$  phase of Ce.

Therefore, the DMFT offers the following scenario for the  $\gamma \rightarrow \alpha$  phase transition. In a large unit cell volume ( $\gamma$ -Ce), the f-electron spectrum is split by the Hubbard repulsion, which results in the appearance of local magnetic moments at cerium sites. As the volume decreases, a quasiparticle at the Fermi energy is formed (the Abrikosov–Saule resonance), which leads to the disappearance of the magnetic moment and a decrease in entropy. The temperature evolution of the quasiparticle peak can be explained by the difference between the Kondo temperatures, which in the  $\alpha$ -phase  $(T_{K,\alpha})$  is much larger than in the  $\gamma$ -phase  $(T_{K,\gamma})$ . In Ref. [96],  $T_{K,\alpha} = 1000$  K and  $T_{K,\gamma} \approx 30$  K; in Ref. [98],  $T_{K,\alpha} = 2100$  K and  $T_{K,\gamma} < 650$  K; estimations of the Kondo temperature from experimental data are  $T_{K,\alpha} = 945$  K,  $T_{K,\gamma} = 95$  K (electron spectroscopy [110]) and  $T_{K,\alpha} = 1800 - 2000$  K,  $T_{K,\gamma} = 60$  K (neutron spectroscopy [111]). Although the Kondo temperature in  $\gamma$ -Ce is very small, the DMFT still considers  $\gamma$ -Ce as a strongly correlated solid. Some differences in the parameters and results in Refs [96, 98] are explained by different methods of solving the single-impurity problem.

Interestingly, the authors of Ref. [97] found some similarity between the DMFT and the Mott-like approach.

Like any other method, the DMFT is not without its assumptions. One of them is the one-electron thermostat serving as a background for 4f-electron correlations. This implies that the 4f states are artificially singled out from the other electron states. Also, the one-electron functions used are obtained within the DFT-LDA, which is known to be an uncontrolled approximation. The other group of approximations is related to the parameter 1/z, which is supposed to be small. This parameter formally prevents the DMFT from being applied to molecules, but it would be very instructive to study how this approximation works for well-known test molecules (for example, in the case of the cerium dimer [34]). In comparison with other 'classic' many-electron methods [32, 33] well known in quantum chemistry, the DMFT is a novel approach and therefore its errors and drawbacks are virtually unknown. Such particularities could be revealed very clearly if the DMFT is compared with the classic quantum chemical approach.

#### 5.3 Attempts to explain lattice anomalies

#### in the $\gamma \rightarrow \alpha$ transition

As we already discussed in Section 4, it was shown in [27] that the cerium lattice plays a significant role in the  $\gamma \rightarrow \alpha$  phase transition: the bulk modulus of  $\gamma$ -Ce softens (Fig. 7) as the pressure approaches the phase transition point [78, 79], and the estimated vibrational entropy change is about half the total entropy change [27].

Before study [27], the role of the cerium lattice in theoretical models was considered insignificant and was often ignored. In recent studies [70] and [89], attempts were made to understand the role of the lattice [27] in the respective frameworks of the empirical Kondo model and the DMFT. In Ref. [89], it was even claimed that the  $\alpha \rightarrow \gamma$  phase transformation is driven by entropy change.

Within the empirical Kondo approach [70], the large entropy lattice contribution is explained by invoking the volume dependence (in the vicinity of the  $\alpha \rightarrow \gamma$  transition, i.e., 28.1–32.5 Å<sup>3</sup>/atom) of the "thermodynamic" Gruneisen parameter

$$\gamma = V \left( \frac{\partial P}{\partial E} \right)_V.$$

For the Gruneisen parameter, two contributions - electronic and lattice  $(\gamma_{lat})$ —were considered. Two very different behaviors of  $\gamma_{lat}$  were then found. The first was obtained from the fit of the Kondo expression of the free energy F(V,T) to the low-temperature isothermal experimental data (with the accuracy of 0.08 GPa). The lattice Gruneisen parameter  $\gamma_{\text{lat}}(V)$  was assumed to be a function of only the volume V. In the range of transitional volumes (28.1-32.5 Å),  $\gamma_{\text{lat}}(V)$  crossed the zero value at  $V = 30 \text{ Å}^3$ , and hence the average value of  $\gamma_{lat}$  was close to zero, and the lattice entropy change was only 2% of the total, which contradicts the experimental estimation in Ref. [27]. However, having postulated a nonlinear dependence (in the spirit of the empirical Kondo approach) of the Debye temperature  $\Theta(V, T)$  on the volume and pressure and rejecting the fits of the isotherms p(V) for the transition, the authors were able to obtain a completely different dependence for the Gruneisen parameter:  $\gamma_{lat}$  had a maximum of 2.7 at V = 31.7 Å<sup>3</sup>, remaining positive, but the quality of the fit decreased to

0.09 GPa. By integrating over the 28.1–32.5 Å<sup>3</sup> volume region, the authors obtained a large value of  $\Delta S_{vib}^{\gamma-\alpha}$  that is in agreement with the experimental data in Ref. [27].

We note that in contrast to the theories of structural phase transitions, elastic anomalies are not intrinsic to the Kondo scenario (see Section 6). In addition, it was recently found in [80] that the Gruneisen parameters  $\gamma_q$  for a number of phonon modes become negative at the X point of the Brillouin zone.

# 6. $\gamma \rightarrow \alpha$ transformation as a hidden structural phase transition

In Refs [73–75, 37], a distinctive approach is presented that considers the  $\gamma \rightarrow \alpha$  phase transition as a hidden structural transformation. We note that its intrinsic feature is the softening of the bulk modulus and elastic anomalies [27, 78] (Section 4). Recently, this was for the first time supported by experiments [28, 29] using the method of time-differential perturbed angular  $\gamma\gamma$  correlations of the <sup>111</sup>Cd probe nuclei (Section 7).

### 6.1 Thermodynamic analysis of Eliashberg and Capellmann

The first doubts about the isostructural nature of the  $\gamma \rightarrow \alpha$  phase transitions were expressed in the work of Eliashberg and Capellmann [73]. Their main idea is that in cerium, instead of the critical point between the  $\gamma$  and  $\alpha$  phases, a 'critical point of second-order transitions' (the definition of Landau and Lifshitz, see Ch. 150 [112]) exists, which later was called the tricritical point. In Ref. [112], it is further noted that such a tricritical point "in a sense is analogous to the usual critical point."

Its properties follow from the expansion of the Gibbs free energy (or the chemical potential,  $\mu$ ) in terms of the order parameter amplitude *u*:

$$\mu(P, T, u) = \mu_0(P, T) + A(P, T) u^2 + B(P, T) u^4 + C(P, T) u^6.$$

At the tricritical point, we have  $A_c = 0$ ,  $B_c = 0$ , and  $C_c = 0$ . The main property of this point is that the line of first-order transitions defined by

$$B < 0, \quad 4AC = B^2$$

continues beyond the tricritical point as a line of second-order transitions given by

$$B > 0$$
,  $A = 0$ .

The conclusion that the  $\gamma - \alpha$  phase boundary continues beyond the tricritical point as a line of second-order transitions was completely new. Notably, it explains the minimum of the cerium melting curve, which approximately lies on a line.

Analyzing further experimental thermodynamic data, the authors of Ref. [73] were able to reconstruct phase transition boundaries, the melting curve, the change in compressibility, and the entropy, which were in good agreement with experimental values.

Probably the most important conclusion that follows from the treatment is that the space symmetry of the  $\alpha$  phase should be lower than the symmetry of the  $\gamma$  phase. In [73], a distorted face-centered cubic lattice with at least two nonequivalent atoms in the primitive unit cell was suggested.



**Figure 8.** The line of the bulk modulus minima in the cerium phase diagram continues beyond the critical point [70]. The black squares are taken from Ref. [70], the grey symbols are measurements of other authors. The white circles are bulk modulus minima above the critical point. Inset: the dependence of the bulk modulus at the temperatures 481, 500, 577, 692, and 775 K.

Eliashberg and Capellmann ascribed the phase instability to the soft transverse mode at the L point of the Brillouin zone [76, 77].

The study by Eliashberg and Capellmann was brought to the attention of experimentalists and prompted updated and more refined X-ray measurements of the  $\alpha$  phase [27,70,113]. But the subsequent X-ray diffraction studies [27, 70, 113] have not revealed a distorted fcc structure in  $\alpha$ -Ce, although a pronounced softening of the bulk modulus on the suggested line of second-order transitions has been emphasized in [70] (Fig. 8).

The idea of a nonisomorphic nature of the  $\gamma \rightarrow \alpha$  transition was independently formulated in Refs [74, 75, 37], where a quadrupolar ordering of the electron density in the  $\alpha$  phase was considered as the driving force for the phase transformation. Although the quadrupolar model can be regarded as a continuation of the approach of Eliashberg and Capellmann, already in the first study [74] it was claimed that there is no distortion of the fcc lattice of cerium nuclei, and all structural changes are associated with the electronic density of valence electrons.

#### 6.2 Quadrupolar model of the $\gamma \rightarrow \alpha$ transition

In Refs [74, 75, 37], the  $\gamma \rightarrow \alpha$  phase transition is considered to be structural, albeit with a very special space symmetry lowering. The main peculiarity is that the suggested symmetry change concerns the electron density but conserves the fcc lattice of cerium nuclei in the  $\alpha$  phase. We recall that it is usually the lattice distortion which indicates crystal symmetry lowering. Its absence, according to the authors, explains why the structural nature of the  $\gamma \rightarrow \alpha$  phase transformation has not been revealed earlier. We can therefore speak of a very specific, or rather a hidden, space symmetry lowering.

The quadrupolar model can be considered in the broad and the narrow sense. In the most general sense, it implies a specific symmetry change that masks the structural phase transition. In the narrow sense, the quadrupolar model is a physical model that takes only some important interactions into account. In that sense, the model is not complete, because it neglects other interactions. In Ref. [74], the intersite Coulomb interaction between f-electrons was considered; in Ref. [75], the intersite Coulomb repulsion of s-, d-, and f-electron densities was introduced; and in Ref. [37], two-electron (f and d) intrasite and intersite repulsions were accounted for. In the last case, the model includes correlation effects, which are omitted in the standard band structure calculations.

The simplest description is in the model of interacting f-electrons. As discussed in Section 2, the low-lying energy spectrum of the cerium dimer is caused by 4f-electron interactions, with the Coulomb repulsion as the most important contribution. The Coulomb repulsion between f-electrons belonging to different sites is *the weakest* among the others (see Fig. 4), but that is why the interaction is responsible for the lowest excitations of the many electron spectrum (see [49]). It can therefore be assumed that the driving force of phase transitions is the Coulomb repulsion of the 4f electrons localized at cerium sites, because a change in their electron density costs little energy. This scenario has been studied in Ref. [74]. The Coulomb interaction between the 4f electrons can be written in terms of the double multipole expansion,

$$U^{ff} = \frac{1}{2} \sum_{n,n'} \sum_{A,A'} \rho_A^{\rm F}(n) \, v_{A,A'}(n-n') \, \rho_{A'}^{\rm F}(n') \,, \tag{3}$$

where  $\Lambda$  stands for  $(l, \tau)$ , with l being the angular index of the multipole expansion and  $\tau = (\Gamma, k)$ , where  $\Gamma$  refers to an irreducible representation of the cubic point group and l labels rows of  $\Gamma$  [114]. The quantity  $\rho_A^{\rm F}(n)$  is the operator of the multipole electron density at the cerium site n and  $v_{A,A'}(n-n')$  is the multipole interaction matrix. Then the authors retain two important groups of terms in Eqn (3): the quadrupole interaction  $(U_{QQ}^{ff}, l = l' = 2)$  and the crystal field contribution (l = 4, l' = 0). After the Fourier transformation,  $U_{\rm QQ}^{ff}$  can be rewritten in terms of Fourier transforms  $\rho_{\rm Q}^{\rm F}({\bf q})$ and  $v_{Q\tau,Q\tau'}(\mathbf{q})$  ( $\tau = 1-5$ ). The 5 × 5 quadrupole matrix  $v_{Q\tau,Q\tau'}(\mathbf{q})$  has negative eigenvalues at some points of the Brillouin zone, which implies an effective attraction between 4f electrons. In particular, a large negative value  $(-\lambda^{X})$  has been found at the X point of the Brillouin zone  $[\mathbf{q}_{\mathbf{X}} = 2\pi/a(1,0,0)]$ . It has two degenerate eigenvectors, which can be expressed through two components of the  $T_{2g}$ symmetry [74]. This effective attraction leads to a phase instability at 86 K, which results in the appearance of the quadrupole electron density and concomitant symmetry lowering. Because the space group of  $\mathbf{q}_{\mathbf{X}}$  involves three rays,  $2\pi/a(1,0,0)$ ,  $2\pi/a(0,1,0)$ , and  $2\pi/a(0,0,1)$ , its electronic mode has six components. Condensation of three out of six density components at  $\mathbf{q}_{\mathrm{X}}$  enables the  $Fm\bar{3}m \rightarrow Pa\bar{3}$  structural phase transition [114–116]. Thus,  $\gamma$ -Ce is identified as the disordered phase (with the order parameter amplitude  $\rho = 0$ ) with the  $Fm\bar{3}m$  space symmetry, whereas  $\alpha$ -Ce is the quadrupolar ordered phase of cubic symmetry but with a different space group, Pa3.

Condensation of a single component of one ray (for example at  $\mathbf{q}_X^x$ ) implies that this component changes sign in real space in going from one crystallographic plane (perpendicular to the *x* axis) to another. Condensation of all three



**Figure 9.** (a) The triple-*q*-antiferroquadrupolar structure (3-q-AFQ) proposed for  $\alpha$ -Ce in Ref. [74]. The quadrupolar (l = 2) functions represent the electron density component of the four  $(4f + 5d6s^2)$  valence electrons. (b) The view along one of the main cube diagonals [111] demonstrating the trigonal point site symmetry  $(S_6)$ . (Figure from Ref. [28].)

components means that the sign changes in going from one plane to another along the x, y, and z axes. Such structures are called triple-q-antiferroquadrupolar or 3-q-AFQ. A close examination shows that the  $Pa\bar{3}$  structure is described by four different sublattices of the simple cubic lattice (Fig. 9). The cerium atoms belonging to the same sublattice are completely equivalent, while cerium atoms of different sublattices are not. The four sublattices  $n_{\rm p}$  contain the following sites (which were completely equivalent in the  $\gamma$  phase): (0, 0, 0), (a/2)(0, 1, 1), (a/2)(1, 0, 1), and (a/2)(1, 1, 1) 0). The symmetry lowering implies that in the ordered phase, at each cerium site, there is only one three-fold symmetry axis  $(C_3)$ , which simultaneously is a main cube diagonal. If the [111] direction is taken as the new z' axis, then the angular component of the quadrupolar density is described by the function  $S_{[111]}(\theta', \varphi') = Y_{\ell=2}^{m=0}(\theta', \varphi')$ , which is aligned along the z' axis. In the x, y, z coordinate system, the angular function is given by

$$S_{[111]}(\theta,\varphi) = \frac{1}{\sqrt{3}} \left( Y_2^{1,s}(\theta,\varphi) + Y_2^{1,c}(\theta,\varphi) + Y_2^{2,s}(\theta,\varphi) \right).$$

We recall that in the fcc structure, there are four three-fold symmetry axes (the four main cube diagonals)  $[\rho_1, \rho_2, \rho_3]$ : [111],  $[\bar{1}\bar{1}1]$ ,  $[1\bar{1}\bar{1}]$ , and  $[\bar{1}1\bar{1}]$ . Hence, in the ordered ( $\alpha$ -Ce) phase, only one out of these four axes remains for each of the four sublattices (see Fig. 9). The angular quadrupolar function at any site can be expressed in the form

$$S(\theta, \varphi) = \rho \left\{ \exp \left[ i \mathbf{q}_{y}^{X} \mathbf{R}(n) \right] Y_{2}^{1,s}(\theta, \varphi) \right. \\ \left. + \exp \left[ i \mathbf{q}_{z}^{X} \mathbf{R}(n) \right] Y_{2}^{1,c}(\theta, \varphi) + \exp \left[ i \mathbf{q}_{x}^{X} \mathbf{R}(n) \right] Y_{2}^{2,s}(\theta, \varphi) \right\},$$

where  $Y_2^{1,s}(\theta, \varphi)$ ,  $Y_2^{1,c}(\theta, \varphi)$ , and  $Y_2^{2,s}(\theta, \varphi)$  (proportional to *yz*, *zx*, and *xy*) are real spherical harmonics [114] and **R**(*n*) is the radius vector of the site *n*. The quadrupole order involves all nonspherical states (i.e., p, d, and f), and therefore, in general, we are speaking of the local quadrupole density component of all four valence cerium electrons [37, 75]. This component is noticeably weaker than the spherically symmetric electronic density present in both  $\gamma$  and  $\alpha$  phases and formed by all 58 cerium electrons.

### 6.3 Volume change and bulk modulus softening in the quadrupolar model

The quadrupolar model was considered for a deformable crystal lattice [74]. The lattice adjusts to the change in electron

density caused by the appearance of quadrupole components, which is a secondary effect. Without going into the details, we note that taking derivatives of Coulomb interactions into account allows obtaining an additional (quadrupole-quadrupole-translation) contribution  $U^{QQT}$  to the Hamiltonian of a deformable crystal lattice, which is bilinear in the order parameter amplitude  $\rho$  (quadrupole) and linear in lattice displacements  $u_{\nu}(\mathbf{q})$  (translation) [74]. This contribution is analogous to the well-known rotation-rotation-translation term  $U^{\text{RRT}}$ , which has been thoroughly studied in the theory of phase transitions of molecular crystals [117, 118]. For example, the compression of the fullerite lattice (in the  $C_{60}$ crystal) at the  $Fm\bar{3}m \rightarrow Pa\bar{3}$  phase transition [119, 120] was considered in Ref. [117]. In the quadrupolar model, the situation in cerium is then quite analogous to the model in [117].

As discussed in Section 6.2, the phase transition itself is driven by the condensation of the order parameter at the X point of the Brillouin zone,  $\mathbf{q}_{\mathbf{X}}$ . For a deformable lattice, the condensation leads to the contribution to the free energy (per atom) given by

$$F^{\text{QQT}}[\rho,\varepsilon] = -2a\Lambda\rho^2(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}), \qquad (4)$$

where  $\varepsilon_{vv}$  are longitudinal strains,  $\rho$  is the quadrupolar order parameter amplitude (see Section 6.2), *a* is the lattice constant, and  $\Lambda$  is a parameter related to derivatives of the Coulomb interaction between quadrupole density components. We note that the special role of phonon modes at the X point of the Brillouin zone was emphasized in recent inelastic X-ray scattering experiments [80]. Combining  $F^{QQT}[\rho, \varepsilon]$  with the elastic lattice contribution  $F^{TT}[\varepsilon]$ , quadratic in  $\varepsilon_{vv}$ , and with the free energy [74], and minimizing the resultant expression with respect to the strain tensor components, we obtain

$$\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{zz} = 8a^{-2}\Lambda\kappa_L\rho^2 < 0, \qquad (5)$$

where  $\kappa_L = (c_{11}^0 + 2c_{12}^0)^{-1}$  is the bare lattice compressibility, and  $c_{11}^0$  and  $c_{12}^0$  are elastic constants. Because  $\Lambda < 0$ , Eqn (7) results in a homogeneous lattice contraction in the ordered  $\alpha$  phase and a concomitant discontinuous decrease in the cubic lattice constant. If only f-electrons are considered, the change in the lattice constant is small ( $\Delta a = -0.002$  Å). It increases by 4.4 if s- and d-electrons are included into the model [75], but the estimation does not take the bulk modulus softening into account (see Section 6.5).

It is also well known [85, 86, 121] that the  $U^{\text{RRT}}$  interaction leads to a softening of the elastic constant:

$$c_{11} = \frac{c_{11}^0}{1 + v^2 \chi / c_{11}^0} \,.$$

Here,  $c_{11}^0$  is the bare elastic constant in the absence of interaction (4),  $\nu$  is the corresponding interaction constant, and  $\chi$  is the static susceptibility, which is proportional to the quadrupole specific heat. In fact, this is a quadrupole analog of the compressible Ising model [85, 86, 121]. We note that this mechanism was indicated in [27] as the most probable one in the  $\gamma \rightarrow \alpha$  transition. Thus, the softening of the bulk modulus [27, 70] and the longitudinal speed of sound [78] at the  $\gamma \rightarrow \alpha$  transition reflects the specific heat increase (in analog with the deformable Ising lattice [85, 86]).

Finally, we note that in Ref. [117], the Clausius– Clapeyron equation was derived and the transition temperature  $T_1$  was shown to be a linear function of the external pressure P with a positive coefficient of proportionality. The corresponding expression for cerium is

$$\frac{\mathrm{d}T_1}{\mathrm{d}P_1} = 4a^{-2}\Lambda\kappa_L x^{(2)}\,,$$

where  $x^{(2)}$  is the one-particle expectation value. This expression accounts for the linear dependence of the  $\gamma/\alpha$  boundary in the P-T diagram of cerium [2].

Thus, the quadrupolar model of the  $\gamma - \alpha$  transition is able to explain many nontrivial effects qualitatively: the volume decrease, the softening of the bulk modulus, and the linear pressure increase of the  $\gamma/\alpha$  boundary in the P-T diagram, although the quantitative agreement is not so good.

### 6.4 Does the nuclear subsystem of $\alpha$ -Ce preserve the fcc lattice in the quadrupolar model?

The conclusion that the fcc symmetry of a nuclear subsystem is preserved at the  $\gamma \rightarrow \alpha$  transition was formulated in Refs [37, 74, 75]. An alternative opinion on this problem presented in referee reports by Yu A Uspenski to this review<sup>1</sup> is based on the following arguments: "Consider the electron density of the  $\alpha$  phase in the form of  $\rho(\mathbf{r}) = \rho_0(\mathbf{r}) + \delta \rho_Q(\mathbf{r})$ , where  $\rho_0(\mathbf{r})$  is a part of the electron density having the same symmetry as in the  $\gamma$  phase, while  $\delta \rho_{\rm O}(\mathbf{r})$  is a perturbation of the density, lowering the symmetry of the electron subsystem. The Coulomb potential (Hartree's potential) associated with the electrons in the  $\alpha$  phase will be  $V(\mathbf{r}) = V_0(\mathbf{r}) + \delta V_0(\mathbf{r})$ , where the potentials  $\rho_0$  and  $\delta V_Q$  are due to  $\rho_0$  and  $\delta \rho_Q$ , respectively. The potential perturbation  $\delta V_Q(\mathbf{r})$  should have the same low symmetry as  $\delta \rho_{\rm O}(\mathbf{r})$ . The electric field associated with  $\delta V_{\rm Q}(\mathbf{r})$  will act on all charges in the system, including electrons and nuclei. Under the action of this field, the nuclei will be displaced from the equilibrium positions and their symmetry will be lowered. Therefore, the symmetry of the electronic and nuclear subsystems should be the same." "The nuclear displacements can be small and difficult for experimental determination but principally nonzero."<sup>2</sup>

To examine the situation, we consider the full potential in the form of a multipole expansion. (The detailed multipole expressions for nonspherical crystal potentials are discussed in Refs [122, 123]). We consider the cerium nucleus at the origin of coordinates and a main cube diagonal as the z axis. According to the quadrupolar model, the full potential  $V(\mathbf{r})$ in  $\alpha$ -Ce then has quadrupole (l = 2) and monopole (l = 0) contributions. The monopole component is also present in  $\gamma$ -Ce. From the equilibrium condition for  $\gamma$ -Ce (a nucleus is at the potential minimum), we obtain

$$V_0(\mathbf{r}) = V_0(r, \theta, \phi) = -C_0 r^2 \qquad (C_0 > 0).$$
(6)

In  $\alpha$ -Ce, there is also the quadrupole density contribution

$$\delta \rho_{\mathcal{O}}(r, \theta, \varphi) = \rho_{\mathcal{O}}(r) Y_{\ell=2}^{m=0}(\theta, \varphi),$$

<sup>1</sup> The name of the referee is given with his permission.

where  $\rho_Q(r)$  is the radial function. The potential corresponding to this density contribution can be found by the multipole expansion [75, 122, 123]:

$$\delta V_{\rm Q}(\mathbf{r}) = \delta V_{\rm Q}(r,\theta,\phi) = \frac{4\pi}{5} \left( \frac{q_2(r)}{r^3} + r^2 q_2'(r) \right) Y_{\ell=2}^{m=0}(\theta,\phi) , \qquad (7)$$

where

$$q_2(r) = \int_0^r \rho_Q(r') r'^4 dr'$$
 and  $q'_2(r) = \int_r^R \rho_Q(r') r'^{-1} dr'.$  (8)

Here,  $q_2(r)$  describes a quadrupole charge located inside a sphere of radius r and  $q'_2(r)$  is an effective quadrupole potential due to the electron density outside the sphere. We note that there are no divergencies at r = 0 because the quadrupole component can be formed by p-, d-, and f-electrons (l = 1, 2, 3), whose wave function in the vicinity of zero behaves as  $r^l$ , and the density behaves as  $r^{2l}$ . Therefore, in the region  $r \approx 0$ , the first term can be omitted (because it gives a small dependence of the  $r^4$  type). The function  $q'_2(r)$  at  $r \approx 0$  can be estimated from above:  $q'_2(r) \approx q'_2(r = 0) = q'_2$ . For potential (7), we then obtain

$$\delta V_{\mathbf{Q}}(r,\theta,\varphi) = C_2 r^2 Y_{\ell=2}^{m=0}(\theta,\varphi) , \qquad (9)$$

where  $C_2 = (4\pi/5) q'_2$ . It follows from the multipole expansion that the contribution from the distant crystal region (the whole crystal except the cerium unit cell at the origin) also has the same functional form (9). Therefore, this contribution can be accounted for by changing the parameter  $C_2$  accordingly.

In  $\alpha$ -Ce, the full potential is  $V(\mathbf{r}) = V_0(\mathbf{r}) + \delta V(\mathbf{r})$ , from which we infer that the minimum at r = 0 is preserved if the condition

$$C_0 > |C_2| \max |Y_{\ell=2}^{m=0}(\theta, \varphi)| = |C_2| \frac{1}{2} \sqrt{\frac{5}{\pi}}$$

is satisfied. This condition holds because the quadrupole component formed by four valence electrons is appreciably smaller than the monopole component formed by all the 58 electrons, i.e,  $C_0 \ge |C_2|$ . Therefore, our opinion is that the fcc lattice of cerium nuclei is preserved in the  $\alpha$  phase.

In connection with this discussion, it is worth noting experimental results on NpO<sub>2</sub> [132], where the situation is somewhat analogous to the  $\gamma \rightarrow \alpha$  transition in cerium (see Sections 6.5 and 6.6.1 for more details). In the lowtemperature ordered phase, a quadrupole component of the electron density appears on the neptunium atoms forming an fcc sublattice, whose symmetry (3-q-AFQ) is very close to the one predicted by the quadrupole model. The quadrupole ordering in NpO<sub>2</sub>, however, does not lead to an experimentally observable deformation of the fcc sublattice of neptunium [18, 132].

#### 6.5 Discussion of the quadrupolar model

The quadrupolar model does predict a volume change in the  $\gamma \rightarrow \alpha$  transition; however, if only the 4f-electron repulsion is included [74], the numerical estimation is an order of magnitude smaller than the experimental value. But we should take the following into account. First, as discussed in Sections 4.1 and 4.2, on approaching the  $\gamma \rightarrow \alpha$  phase

<sup>&</sup>lt;sup>2</sup> These arguments were expressed to the authors in the discussion of their work at a seminar of the Tamm Division of Theoretical Physics, Lebedev Physical Institute. We also note that according to the symmetry principle formulated by P Curie in 1894, a crystal under an external perturbation (cause) changes its point symmetry such that only the symmetry operations common with the symmetry operations of the cause are preserved.

boundary, softening of certain phonon modes and a substantial decrease (see Figs 7 and 8) in the bulk modulus [27, 70, 76–78] are observed. Such a strong softening inevitably leads to a corresponding increase in lattice compression. Also, as discussed in Section 2 (see Fig. 4), the phase transition affects the conduction electrons, which are responsible for metallic bonding. We note that the interaction between the 4f electrons should be regarded rather as a precursor [75, 37], which prompts a chain of electron reconstructions of 5d and 6s states responsible for the metallic bond in cerium (see Section 2). We should also keep in mind that a large volume change occurs only in a limited area of the phase diagram of cerium, specifically in the region of low temperatures and pressures, where the influence of metallic 5d and 6s states is probably more pronounced, while in the vicinity of the critical

It is conceivable that only f-states are effective in that area. We also note that according to Eliashberg and Capellmann [73] (see Section 5.1), there is no true critical point. Because the symmetries of two phases differ, the interphase boundary continues up to the melting curve (see Fig. 1). The experimental information on the phase transition in this area (i.e., above the tricritical point and below the melting curve minimum) is dubious. Indeed, in Fig. 8 (Ref. [70]), the bulk modulus demonstrates a characteristic V-shaped dependence on pressure, which implies a pronounced softening at the curve minimum even at a temperature of 775 K and pressure of 2.5 GPa, although this point (Fig. 1) is situated far from the tricritical point and close to the melting curve minimum. Therefore, the dashed line can be an interphase boundary of second-order transitions (as assumed in Ref. [73]) or first-order transitions with small order parameter discontinuities [74].

point and below it, a negligible change in volume is observed.

The quadrupolar model can describe the crystal field, the phase transition, symmetry lowering, and lattice displacements on equal footing. However, in the mean-field approximation [74], the magnetic susceptibility of a single 4f electron localized at a cerium site is bound to follow the Curie (or Curie–Weiss) law. In practice, as discussed in Section 2, the 4f electron always interacts with 5d and 6s electrons at the same site through the multipole Coulomb repulsion (so-called Hund interaction) [37, 38], and hence 4f, 5d, and 6s states are correlated even in the  $\gamma$ -phase (see Table 4). Taking this effect into account allows explaining the change in the magnetic moment of the ground state [37, 38, 124]. To calculate this effect with confidence is next to impossible, because it requires the computation of the many-electron energy spectrum with a very high accuracy.

Of course, the disappearance of magnetic moments at the  $\gamma \rightarrow \alpha$  phase transition can be described by Kondo-type models [107]. But the symmetry lowering considered in the quadrupolar model in principle allows obtaining this effect solely from the group-symmetry arguments [29, 37, 38, 124]. This mechanism is possible if, as a result of symmetry lowering, the magnetic state of  $\gamma$ -Ce splits into several sublevels and the lowest nonmagnetic sublevel (singlet) then becomes the ground state of the  $\alpha$  phase [38,124].

We have already emphasized that although the  $\gamma \rightarrow \alpha$ phase transition is structural with the  $(Fm\bar{3}m \rightarrow Pa\bar{3})$ symmetry lowering according to the quadrupolar model, it looks different experimentally. The main reason is that before and after the phase transformation, the cerium nuclei form an fcc lattice, which hinders experimental identification of the true symmetry change. On the other hand, the  $Pa\bar{3}$  space symmetry is often found in molecular crystals. For example, a phase of this symmetry is observed in molecular orthohydrogen [125], in the C<sub>60</sub> fullerite [126, 127], and in molecular nitrogen (a phase) [128]. In fact, the quadrupolar model [74] was inspired by the theory [129, 130] of the  $Fm\bar{3}m \rightarrow Pa\bar{3}$ phase transition in the C<sub>60</sub> fullerite. However, in all molecular solids, the transformation to the  $Pa\bar{3}$ -structure implies an ordering of nuclei, and it can therefore be identified relatively easy. This is not so in metals with cubic lattices, and the recognition of the 3-q-AFQ structure becomes a nontrivial experimental problem. Nevertheless, hidden structural phase transitions directly related to the quadrupole density ordering have been found in some rare earth compounds (see Section 6.5.1). Among them, the most remarkable example is perhaps NpO<sub>2</sub> [19, 131, 132]. For a long time, NpO<sub>2</sub> had been thought to undergo an isostructural phase transition at 25.5 K. But when the oxide was studied by resonant X-ray spectroscopy, it was found that the low-temperature phase has a hidden order related with the quadrupole ordering of the electron density [132]. It turned out that the phase transition in NpO<sub>2</sub> is of the  $Fm\bar{3}m \rightarrow Pn\bar{3}m$  type, and the symmetry of the ordered phase  $(Pn\bar{3}m)$  is very close [133] to Pa3 as suggested by the quadrupolar model [74] (Fig. 10 and Section 7). Thus, in NpO<sub>2</sub>, an effect was observed that was expected to occur in pristine crystalline cerium. In principle, additional reflections from the cerium electron density could be found similarly in X-ray diffraction experiments with a synchrotron radiation source, especially because a new resonant X-ray scattering technique-RXS-has been developed recently [134–136]. However, recent experimental data in support of the quadrupole order in  $\alpha$ -Ce have been obtained differently by the nuclear method of perturbed angular correlations [28, 29] (Section 7).

Finally, we would remark on the relation between quadrupolar and orbital ordering [137]. If there is only one valence electron at a site, the quadrupolar ordering is equivalent to the orbital one. But if there are two or more electrons per site, it is impossible to extract only one orbital, because various orbitals of different electrons are mixed (e.g., as in adding two angular momenta). We believe that the concept of quadrupolar ordering is more correct, because, first, unlike the orbital, the electron density is an observable quantity and, second, it is the density which is usually identified with the order parameter in the Landau theory of phase transitions [112].



**Figure 10.** Quadrupolar structures  $Pn\overline{3}m$  (NpO<sub>2</sub>) and  $Pa\overline{3}$  (from [133]). In both structures, the point site symmetry of the rhombohedral (trigonal) system is  $S_6 = C_3 \times i$ . The structures differ by the distribution of the quadrupole functions among four crystal sublattices. The  $Pn\overline{3}m$  space group has three mirror planes, one of which is explicitly shown.

### 6.6 Phase transitions with the quadrupolar ordering of electron density

6.6.1 Hidden structural phase transition in NpO2. Already in 1953, specific heat capacity measurements in NpO<sub>2</sub> at the temperature  $T_Q = 25.5$  K revealed a phase transition of an unknown nature [19], which became the subject of theoretical and experimental study [138-140]. Because no visible structural distortion was found [139], for many years the phase change in NpO<sub>2</sub> was considered isostructural, like the  $\gamma \rightarrow \alpha$ transition in pristine cerium. The disappearance of the localized magnetic moments in the low-temperature (ordered) phase further strengthened the analogy. To account for the magnetic effect, Santini and Amoretti introduced an octupole magnetic order parameter [140]. The puzzle was solved in 2002, when the phase transition was studied by resonant X-ray scattering experiments performed at the Np  $M_{IV}$  and  $M_V$  edges [132]. It turned out that superlattice peaks indicative of a long-range order of neptunium quadrupoles appear in NpO<sub>2</sub> below  $T_Q$ . The symmetry of the quadrupolar phase  $Pn\bar{3}m$  is very close to  $Pa\bar{3}$  (see Fig. 10). (We recall that the  $Fm\bar{3}m \rightarrow Pa\bar{3}$  symmetry lowering was previously suggested in Ref. [74] for the description of the  $\gamma \rightarrow \alpha$  phase transition in cerium.) Figure 10 illustrates that both space symmetries belong to the 3-q-AFQ family and differ only by the correspondence among four quadrupolar components and four cubic sublattices [133] (Fig. 10). (The scheme of condensation to the  $Pn\bar{3}m$ symmetry is given in Ref. [133].) The NpO<sub>2</sub> story demonstrates that the structural transition scenario for the  $\gamma \rightarrow \alpha$ transition in cerium is very probable.

6.6.2 Quadrupole transitions in CeB<sub>6</sub>, DyB<sub>2</sub>C<sub>2</sub>, UPd<sub>3</sub>, TmTe, and other compounds. Cerium hexaboride CeB<sub>6</sub> is a wellknown example of a cubic compound (the  $Pm\bar{3}m$  space symmetry) where the quadrupole transition occurs at a temperature  $T < T_Q = 3.3$  K (in a zero magnetic field) (see the review of recent work in Ref. [131]). With increasing the magnetic field,  $T_Q$  also increases, reaching 10 K at 30 T. Recently, the phase transition was studied by means of the novel technique of resonant X-ray spectroscopy [134]. With it, the appearance of the (1/2, 1/2, 1/2) superlattice diffraction peak in CeB<sub>6</sub> [141] and the (h/2, h/2, h/2) reflections (h is odd) in Ce<sub>0.7</sub>La<sub>0.3</sub>B<sub>6</sub> [142, 143] were detected (in the absence of a magnetic field).

There is also a strong indication that the magnetic field can suppress the  $\gamma \rightarrow \alpha$  phase transition in pristine cerium. At least, this effect (the complete suppression of the transition in the 56 magnetic field) was recently found in Ce<sub>0.8</sub>La<sub>0.1</sub>Th<sub>0.1</sub>, where the  $\gamma \rightarrow \alpha$  transition is shifted to T = 47 K [144].

Quadrupole transitions have been observed in the compounds  $RB_2C_2$  (R = Dy, Ho, Tb), UPd<sub>3</sub>, and others [131]. The most popular among them is DyB<sub>2</sub>C<sub>2</sub> with the quadrupolar ordering temperature  $T_Q = 24.7$  K (the  $P4_2/mnm$  space symmetry). As temperature decreases below  $T_Q$ , the superlattice peaks (h/2, k/2, 9/2) of the reciprocal lattice develop in DyB<sub>2</sub>C<sub>2</sub> [145] and the (1,0,3) reflection in UPd<sub>3</sub> [146].

An antiferro-quadrupolar ordering ( $T_Q = 1.8$  K) was found in TmTe [147]. Thulium, with one localized 4f hole at each Tm site, is a relatively simple electron system [148]. The peculiarities of the quadrupolar ordering in an external magnetic field were studied by neutron spectroscopy, which registered the (1/2, 1/2, 1/2) Bragg reflection of the reciprocal lattice [149].

We note that the appearance of superlattice peaks in all these compounds is in fact an indication of crystal symmetry lowering. The quadrupolar ordering is nothing but a lowtemperature phase transition. A change in structure and symmetry of the local environment of a magnetic atom (with an open electron shell) can result in magnetic effects and magnetic ordering. Indeed, the quadrupole phase transition is very often followed by magnetic ordering at a certain temperature  $T_{\rm M}$  that is lower than  $T_{\rm O}$ . In CeB<sub>6</sub> and DyB<sub>2</sub>C<sub>2</sub>, that is the antiferromagnetic ordering. The fact that  $T_{\rm M} < T_{\rm O}$ implies that the quadrupole order parameter is primary. The scenario where the magnetic order is induced by a change in the crystal structure seems crucial and is quite general in this situation. Another illustration of this observation is the well-known fullerene compound TDAE-C<sub>60</sub> (the only organic compound displaying magnetic order below 16 K). In TDAE-C<sub>60</sub>, two stable phases  $-\alpha$  and  $\alpha'$  — were found that differ by the orientation of the  $C_{60}$  fullerene molecule. While the  $\alpha$  phase is ferromagnetic with the critical temperature  $T_{\rm M} = 16$  K, its counterpart  $\alpha'$  is found to be nonmagnetic [150].

Experimental aspects of quadrupolar order in TmCu, PrPb<sub>3</sub>, TbP, DySb, ErAl<sub>2</sub>, TmGa<sub>3</sub>, CeMg, and CeZn and related phenomena are discussed in reviews [151, 152]. According to the authors of [152], interactions of the quadrupole electronic density and induced magnetic moments with the crystal lattice (magnetoelastic interactions) can lead to nonlinear magnetization effects or so-called metamagnetic transitions.

#### 7. Evolution of the electric field gradients on probe <sup>111</sup>Cd nuclei in the cerium lattice

Quadrupolar ordering in a number of compounds (NpO<sub>2</sub> [132], CeB<sub>6</sub>, DyB<sub>2</sub>C<sub>2</sub>, UPd<sub>3</sub> and others [131]) has been detected experimentally by resonant X-ray diffraction using synchrotron radiation. Nevertheless, the experimental identification of the  $\gamma \rightarrow \alpha$  transformation in cerium as a structural phase transition with symmetry lowering is a formidable task.

First of all, we note the weak scattering intensity expected from the quadrupole electron density components of cerium and the unusual domain pattern (8 types of domains for *Pa3*) imitating the fcc structure. Unfortunately, there are also other technical challenges. It is quite difficult to carry out X-ray scattering under pressure. If, instead of applying external pressure, a cerium sample is cooled, then the  $\gamma \rightarrow \alpha$  transition overlaps with other phase transformations  $(\gamma \rightarrow \beta \text{ and }$  $\beta \rightarrow \alpha$ ). The intermediate  $\beta$ -phase (dhcp) is noncubic and obtained by glide motion of some (111)-planes (see the details of this martensitic transition in Section 8). Afterwards, it is not possible to eliminate the  $\beta$  phase, and at low temperatures the sample is a mixture of  $\beta$ -Ce and  $\alpha$ -Ce. Another complication is related to the large volume change at the  $\gamma \rightarrow \alpha$ transition. If the sample is a single crystal, numerous cracks appearing as a result of volume change can simply destroy it. In Refs [2, 44], the following approach was used: first,  $\alpha$ -Ce was reached by compressing the sample to 1 GPa at room temperature, then it was cooled to liquid-nitrogen temperature, and finally the pressure was released. In other experimental works [63, 111, 135], to eliminate the parasitic  $\beta$  phase, the cerium sample was doped by 7 and even 10 at.% Sc [62].

Notwithstanding all these complications, the 3-*q*-AFQ quadrupolar order can be probed practically directly by

another experimental method [28, 29], the time-differential perturbed angular correlation (TDPAC) technique [153, 154]. TDPAC belongs to the methods of nuclear spectroscopy where the electric field gradient (EFG) is measured at nuclear probes introduced at the crystal lattice sites [155]. The <sup>111</sup>In/<sup>111</sup>Cd nuclei were used as probes. Measuring the electric field gradient through hyperfine quadrupolar interactions in <sup>111</sup>In/<sup>111</sup>Cd nuclei as a function of temperature and pressure [153-155] yields information about the physical properties of rare earth crystals [156, 157]. Hyperfine quadrupole interactions are used in many nuclear methods of solid state physics, for example, in nuclear quadrupole resonance spectroscopy (NQR) and in Mössbauer spectroscopy [155]. TDPAC spectroscopy, in particular, has the following advantages: (1) a small amount of impurity nuclei suffices for the measurements, and (2) in contract to NQR, it is not limited to low temperatures. In the best cases, TDPAC approaches the accuracy of NQR.

In studies [28, 29], the 171–245 keV energy cascade in the <sup>111</sup>Cd nucleus was used, which occurs after the electron capture decay of the <sup>111</sup>In nucleus. In turn, the radioactive <sup>111</sup>In isotope (2.8 day half-life) is produced as a result of the <sup>109</sup>Ag  $\xrightarrow{\alpha, 2n}$  <sup>111</sup>In reaction by irradiating a silver foil by a 32 MeV  $\alpha$ -beam. Nuclear <sup>111</sup>In probes were introduced in the cerium lattice by melting irradiated silver foil (about 0.1 mg) with cerium powder (500 mg) in a special chamber under a pressure of 8 GPa. The main feature of the TDPAC setup is that it allows carrying out measurements under external pressure. To the best of our knowledge, it is currently the only working TDPAC setup with that option. Other experimental details are given in Refs [158–160].

Measurements were performed on polycrystalline samples of cerium metal (99.98% purity) at room temperature under the pressure ranging from the atmospheric value up to 8 GPa. In this range of pressures, the cerium sample consecutively transforms into the following phases:  $\gamma$ ,  $\alpha$ ,  $\alpha''$ ,  $\alpha'$ . The last phase ( $\alpha$ -U-type  $\alpha'$  [6]) appears because the sample was subjected to heat treatment under pressure in the process of melting with a piece of radioactive silver foil [8].

We note that before studies [28, 29], the TDPAC study of cerium was limited to the  $\beta$  phase [161]. The main reason for this is that in the field of the cubic point symmetry (for example, at any site of the fcc lattice), there is no quadrupole component in the electric crystal field expansion and therefore no EFG. Indeed, it is well known that the first nontrivial angular component in the fcc lattice is given by the cubic spherical harmonic  $K_{\ell=4}(\theta, \varphi)$  with the multipole index  $\ell = 4$  (see, e.g., Ref. [114]). This implies that all components with  $\ell = 1, 2, 3$  are zero. Because the EFG tensor  $V_{ij}$  is described by the multipole index  $\ell = 2$ , it follows that  $V_{ij} = 0$ , and the TDPAC method is ineffective, because it gives no information on the cubic crystal field.

The disappearance of the electric field gradient in the fcc lattice can be observed experimentally. Such data (at the <sup>111</sup>Cd probe nuclei in the thallium lattice) are reported in [162]. At atmospheric pressure, the thallium lattice has the hexagonal close-packed structure (the  $P6_3/mmc$  space group), in which the cadmium probes register an electric field gradient of 8.0(4) MHz [162]. With increasing pressure, the quadrupole frequency  $v_Q$  (or EFG) slowly and monotonically decreases to 6.1(5) MHz (at P = 3.5 GPa), but at a slightly increased pressure (P = 3.7 GPa), a structural phase transition to the fcc structure occurs and the EFG drops to zero (0.0(4) MHz) [162].

This effect offers a unique way to check the isostructural feature of the  $\gamma \rightarrow \alpha$  phase transition in cerium. If the  $\gamma \rightarrow \alpha$  transformation is truly isostructual, that is, if the  $\gamma$  and  $\alpha$  phases are characterized by the same cubic point group, then the gradient should be zero,  $V_{ij} = 0$ , in both phases (in practice,  $V_{ij} \approx 0$ ). However, it has turned out that  $V_{ij} \approx 0$  only in the  $\gamma$  phase, whereas  $V_{ij} \neq 0$  in the  $\alpha$  phase [28, 29]. This implies the appearance of a quadrupole component of the electron density at the <sup>111</sup>Cd probe sites and an effective crystal symmetry lowering of the cerium sample. Below, we discuss the results of the experiments in [28, 29] in more detail.

In the  $\gamma$  phase at atmospheric pressure,  $v_O(\gamma) = 3$  MHz [28, 161]. This is practically the background level (Fig. 11 and Table 7). The value is relatively large, and we discuss it in what follows. From general considerations, we can expect approximately the same frequency (EFG) in  $\alpha$ -Ce, whereas it has been found that  $v_{O}(\alpha) = 11$  MHz, which is 3.7 times higher. EFG measured under pressures from the atmospheric value to 8 GPa [28] is reproduced in Fig. 11 and Table 7. We note that the EFG in  $\alpha$ -Ce is comparable to the EFG in other noncubic phases ( $\beta$  and  $\alpha''$ ) that border  $\alpha$ -Ce in the P-Tphase diagram. Thus, the quadrupole electron density component in  $\alpha$ -Ce is approximately the same as in *other* noncubic phases. This experimental finding unambiguously indicates that the  $\gamma \rightarrow \alpha$  transition in cerium is not isostructural, and the symmetry of the  $\alpha$  phase differs from that of the  $\gamma$  phase (*Fm3m*). Previously, a 3-q-AFQ order was predicted



**Figure 11.** Pressure dependence (at room temperature) of the nuclear quadrupole frequency ( $v_Q$ , left axis) and the electric field gradient ( $V_{zz}$ , right axis) at <sup>111</sup>Cd probe nuclei in cerium lattice crystal sites. The results of TDPAC measurements are from Refs [28, 29], data for  $\beta$ -Ce are from Ref. [161].

**Table 7.** The electric field gradient  $V_{zz}$  (the quadrupolar frequency  $v_Q$ ) and the asymmetry parameter  $\eta$  at the probe <sup>111</sup>Cd nuclei in the cerium lattice at room temperature under pressure (*P*). (Data from Refs [28, 29].)

P, GPa	$v_Q, MHz$	η	$V_{zz}, 10^{21} \text{ V m}^{-2}$
0	3.0(5)	0	0.15(3)
1.8	11(1)	0	0.55(5)
3.1	10.9(6)	0	0.54(3)
3.9	10.9(9)	0	0.54(4)
4.4	9.8(9)	0	0.49(4)
5.3	15(1)	0	0.75(5)
6.2	15.8(6)	0	0.79(3)
7.8	21.6(5)	0.52(5)	1.08(3)

in the quadrupole model [74, 75]. Unfortunately, TDPAC spectroscopy cannot determine the exact space group for the  $\alpha$  phase. Possible candidates here are  $Pa\bar{3}$  and  $Pn\bar{3}m$ .

Figure 11 indicates that in addition to the  $\gamma \rightarrow \alpha$  transformation, there are two other jumps of the EFG at pressures 5 and 7.5 GPa. They correspond to two other phase changes,  $\alpha \rightarrow \alpha''$  and  $\alpha'' \rightarrow \alpha'$  (see Section 9). In the case of  $\alpha'$ -Ce, a nonzero asymmetry parameter of the EFG,  $\eta = 0.52$ , was found (Table 7), which is characteristic of  $\alpha$ -U structures. (In particular,  $\eta = 1$  in the  $\alpha$  phase of uranium [163].)

In the course of publication of [28], the referee pointed out that almost all TDPAC spectra R(t) were obtained during the observation time t < T, where T is the period of TDPAC oscillations, which reduces the accuracy of measurements. This was certainly true; furthermore, some additional technical difficulties were caused by applying external pressure [160,164]. However, the same situation (t < T) was observed for the <sup>111</sup>Cd nuclei in thallium, but the hcp  $\rightarrow$  fcc transition was clearly detected there [162]. The t < T relation is caused by a low quadrupole frequency: 6-8 MHz in Tl [162] and 10 MHz in Ce [28, 161]. As pointed out in Ref. [28], in the case of cerium, measurements were carried out with several samples. The EFG jumps were observed both with increasing pressure  $(\gamma \rightarrow \alpha)$  and with decreasing it  $(\alpha \rightarrow \gamma)$ , and hence it certainly follows from our TDPAC experience that the effect of quadrupole ordering does occur in  $\alpha$ -Ce.

There was also concern caused by the relatively large value of the EFG in the  $\gamma$  phase (3 MHz). This is not a simple question. It should be noted that a small nonzero gradient at <sup>111</sup>Cd probes is detected for all cubic crystals, but in cerium it is somewhat larger than the typical value. However, the 3 MHz gradient and the TDPAC spectrum of  $\gamma$ -Ce in Ref. [28] practically coincide with the spectrum and  $v_0$ found in [161]. On the other hand, in a number of cerium samples in Ref. [28], a smaller value of  $v_{\rm O}(\gamma)$  was detected, which shows that  $v_Q(\gamma)$  depends on the sample quality and prehistory. We mention the factors that could produce a nonzero value: (1) the structure of domains and polycrystalite grains, (2) other phase nucleations (for example,  $\beta$ -Ce), and (3) small local strains caused by the replacement of Ce with Cd. Such replacements induce small electric quadrupole moments, which can cause their local freezing [165]. The last factor is inherent in the experimental method and cannot be excluded.

Summarizing,  $v_Q(\gamma)$  should be considered as the background level, which we have to subtract from the EFG of other phases. In any case, the almost fourfold increase in  $v_Q$  at the  $\gamma \rightarrow \alpha$  phase transition cannot be explained within the isostructural paradigm.

# 8. Peculiarities of the electronic structure of $\beta$ -Ce and $\delta$ -Ce

#### 8.1 β-Ce (double hexagonal close-packed structure, dhcp)

The transformation of the fcc structure of  $\gamma$ -cerium to the dhcp structure of  $\beta$ -cerium is martensitic. It depends on the purity and the grain size, proceeds very slowly, and never fully finishes. The amount of the  $\beta$  phase in a sample depends on (1) the cooling rate, (2) the temperature to which the sample is cooled, and (3) the number of cooling-heating cycles. The start of the transformation on cooling (i.e.,  $\gamma \rightarrow \beta$ ) is in the temperature range 240–290 K, and on heating ( $\beta \rightarrow \gamma$ ), at 373-451 K [2]. A 20-year study by Gschneidner et al. puts the low boundary of the transformation at 283 K [166]. Interestingly, the  $\gamma \rightarrow \beta$  transition is accompanied by a small volume increase (1.2%). As a result, the specific volume of  $\beta$ -Ce is slightly larger than the volume of the  $\delta$  phase (0.2%) and is the largest among all cerium allotropies (see Table 2). In  $\beta$ -Ce, the closest distances between cerium atoms belonging to neighboring hexagonal planes slightly decrease (0.05%), while distances within the planes increase (0.88%) in comparison with the closest distances in  $\gamma$ -Ce (see Table 2). (The lattice constants are taken from Ref. [16].) More details about the transformation can be found in review [2].

A dislocation model for the mechanism of the  $\gamma \rightarrow \beta$ transformation in cerium was proposed in [167]. It is well known that in the fcc lattice, the close-packed (111) planes (perpendicular to the [111] vector) form the layering ...ABCABC... sequence (Fig. 12). According to McHargue and Yakel's mechanism [167], two of these planes, e.g., C and A, transform as a result of two glide motions into respective planes A and C. The next two planes, which are A and B, remain in their positions (see Fig. 12). The next two planes, C and A, again undergo glide displacements and become A and C, and so on. The resultant packing sequence changes to ...ABACABAC..., which corresponds to the dhcp layering (see Fig. 12). We note that there are two nonequivalent cerium sites in the dhcp structure, and hence the transformation certainly involves a symmetry lowering. It is often said that the sites of A-type planes are in the 'cubic' (i.e., CAB) environment, because the neighboring planes are C- and B-type, while the cerium sites in C- and B-planes (ACA or ABA) are in the hexagonal environment. We must keep in mind, however, that because the  $\beta$ -phase ratio c/2a = 1.611differs from the cubic one  $(c/a = \sqrt{8/3} \approx 1.633)$ , the exact point symmetry there is not cubic. In particular, there is only one three-fold symmetry axis at the A sites. We also note that the planes C and B can be considered mirror-symmetry planes, and the dhcp structure can be viewed as an ideal



**Figure 12.** The formation of the double hexagonal structure (dhcp,  $\beta$ -Ce) from the face centered cubic lattice (fcc,  $\gamma$ -Ce). (a) the sequence of the (111)-layers in the fcc lattice (ABCABC); (b) the sequence of the (111)-layers in the dhcp lattice (ABACABAC); (c) glide planes transforming the fcc sequence (top) to the dhcp sequence (bottom).

twinned crystal. The martensitic character of the transformation is supported by the observation that in the range 196– 500 K, plastic deformations assist the  $\gamma \rightarrow \beta$  transformation. Obviously, the appearance of numerous glide motions leads to appreciable microdeformations in the crystal grains.

Although the rate of the  $\gamma \rightarrow \beta$  change is very low, the transformation cannot be avoided, even on fast cooling (quenching). This hinders the study of another phase transition,  $\gamma$ -Ce (fcc)  $\rightarrow \alpha$ -Ce (cubic), which is of fundamental interest. From the standpoint of the  $\gamma \rightarrow \alpha$  transition, the phase transformation to the  $\beta$  phase at low temperatures is a parasitic process that should be completely suppressed. As a solution to this problem, in a number of studies [62, 63, 111, 135] cerium samples were doped with scandium:  $Ce_{1-x}Sc_x$ , where x = 0.07 [63, 111, 135] or x = 0.1 [62]. Atoms of trivalent scandium have a smaller metallic radius (1.62 Å), which results in a smaller lattice constant of the  $Ce_{1-x}Sc_x$  fcc crystal. This is equivalent to an effective external pressure  $P_{\rm eff}$ applied to shift the  $\gamma \rightarrow \alpha$  transition to a phase diagram region where the intermediate  $\beta$  phase is absent. However, the scandium amount is not negligible, and these samples cannot be regarded as pristine cerium. Such cerium-scandium compounds  $Ce_{1-x}Sc_x$  are not always suitable for studies of subtle effects.

Recently, refined data on  $\beta$ -Ce and  $\gamma$ -Ce have been reported [166, 168–170]. The electron specific heat ( $\gamma$ ) is  $(7.0 \pm 0.1) \times 10^{-3}$  J mole<sup>-1</sup> K<sup>-2</sup> for  $\beta$ -Ce and  $(6.2 \pm 0.8) \times$  $10^{-3}$  J mole<sup>-1</sup> K<sup>-2</sup> for  $\gamma$ -Ce. Thus, earlier values [2] decreased. In Ref. [166], the entropy change  $\Delta S^{\beta-\gamma} = 0.05k_{\rm B}$ per cerium atom was obtained from the latent heat of the  $\beta \rightarrow \gamma$  transformation at 420 K. There are two contributions to the entropy change, one from the lattice,  $\Delta S_{\rm el}^{\beta-\gamma} =$  $= (0.09 \pm 0.05) k_{\rm B}$ , and the other electronic,  $\Delta S_{\rm el}^{\beta-\gamma} =$  $-(0.04 \pm 0.05) k_{\rm B}$  [169]. The result shows that the lattice term causing the softening of the phonon spectrum in  $\gamma$ -Ce is the leading, while the electronic contribution acts in the opposite direction [169], destabilizing the  $\beta \rightarrow \gamma$  transition.

Another anomaly of the  $\beta$  phase that we have mentioned above is that its volume is larger than the volume of any other cerium phase (Table 2). This is an indication that the very existence of the  $\beta$  phase is related to its intermediate role in the  $\gamma \rightarrow \alpha$  transition.  $\beta$ -Ce is stabilized by polycrystalline grains, interphase boundaries, twinings, and other defects. Indeed, in a single crystal, the volume change at the  $\gamma \rightarrow \alpha$  transition accompanied by considerable strains cleaves the crystal. In polycrystals, the same elastic strains between grains and domains of the  $\alpha$  phase move some of the (111) planes to the intermediate  $\beta$ -structure. It then follows that any defects, for example in the area between domains and other phases, are partially compensated and softened by the growth of grains in the  $\beta$  phase with a large volume per atom. This observation explains the well-known fact that the amount of  $\beta$ -Ce on cooling from  $\gamma$ -Ce to  $\alpha$ -Ce is 20–30% [2], and can be increased by multiple  $\gamma$ -Ce  $\rightarrow$  $\alpha$ -Ce  $\rightarrow \gamma$ -Ce cycling.

Because of the nature of the  $\beta$  phase, the growth of a  $\beta$ -Ce single crystal seems impossible. Nevertheless, it has turned out that a single-crystal  $\beta$  phase can be obtained by the molecular epitaxy method on an Nd surface, which stabilizes it down to low temperatures (T = 2 K) [171]. In Ref. [171], such an epitaxial  $\beta$  phase containing 60 layers of Ce<sub>30</sub>/Nd<sub>10</sub> was studied in detail. The lattice parameters are a=3.664(3) Å and c=2.970(3) Å (in niobium, c=2.949(3) Å), implying a small compression within the hexagonal planes (0.5%) and a



**Figure 13.** Antiferromagnetic transverse ordering in  $\beta$ -Ce. (Data for the epitaxial phase of  $\beta$ -Ce, Ref. [171], and Ce<sub>0.75</sub>Y<sub>0.25</sub>, Ref. [173].)

small expansion between the planes (0.2%) in comparison with the bulk  $\beta$  phase [16]. Unlike the bulk phase, the epitaxial  $\beta$  phase (e- $\beta$ -Ce) does not transform to  $\alpha$ -Ce. Moreover, the epitaxial  $\gamma$ -Ce does not undergo the transition to e- $\beta$ -Ce on cooling. Instead, at T = 120 K, e- $\gamma$ -Ce (Ce<sub>30</sub>/Nd<sub>10</sub>) transforms into a phase with the samarium structure, which is very typical of 5d metals [172]. This is another indication of the very important relation between  $\beta$ -Ce and the  $\gamma \rightarrow \alpha$ transition in a polycrystalline sample, underlining the decisive role of elastic strains for the stabilization of the  $\beta$  phase.

Neutron diffraction measurements of the magnetic order in e- $\beta$ -Ce (at T = 7 K [173]) confirmed the results reported previously for the Ce<sub>x</sub>Y<sub>1-x</sub> compounds [174,175]. The antiferromagnetism is related to the transverse order (along one of the *a* directions of the hexagonal lattice) of the 0.1µ<sub>B</sub> magnetic moments. (In Ce<sub>x</sub>Y<sub>1-x</sub>, the magnetic moments are larger [174, 175].) The sign alternation vector (the [1/2, 0, 0] point of the Brillouin zone) is perpendicular to the magnetic moments (Fig. 13). The antiferromagnetic ground state of  $\beta$ -Ce (with 1.1µ<sub>B</sub> magnetic moments) is reproduced by band structure calculations only in the LDA + U approximation, while the standard density functional calculations (LDA or GGA approximation) predict the ferromagnetic ground state [175].

#### 8.2 $\delta$ -Ce (body-centered cubic structure, bcc)

In contrast to close-packed fcc and dhcp phases, the bodycentered cubic (bcc) lattice is an open structure with large volume in the interstitial region. Bcc structures are characteristic of high-temperature phases of transitional elements with a partially filled d-shell. On cooling, the phases typically transforms to close-packed structures, but this instability rapidly disappears with increasing the d-shell occupation. Bcc phases are also found in rare earth elements, but there they exist in a narrow temperature range of about 10 K. In cerium, this temperature range is much larger (69 K), which also characterizes it as a d-element. (The important contribution of d-electrons to the metal bond of cerium is discussed in detail in Section 2.) Thus, on cooling from the cerium melt,

**Table 8.** Force constants  $\Phi_{\alpha\beta}(\mathbf{R}_n \text{ (in n m}^{-1} \text{ or } 10^3 \text{ dynes cm}^{-1})$  of  $\delta$ -Ce in the Born–von Kárman model with five nearest coordination shells obtained by fitting the phonon spectrum at 1036 [82]. *N* is the number of atoms in a shell,  $\alpha(\beta) = x, y, z$ .

	$\mathbf{R}_n$	N	$arPsi_{lphaeta}({f R}_n)$
1	a(1/2, 1/2, 1/2)	8	$\Phi_{xx} = 2.945,  \Phi_{xy} = 3.563$
2	a(1,0,0)	6	$\Phi_{xx} = 2.313,  \Phi_{yy} = -0.856$
3	a(1, 1, 0)	12	$\Phi_{xx} = 0.048,  \Phi_{zz} = 0.171, \ \Phi_{xy} = 0.346$
4	<i>a</i> (3/2, 1/2, 1/2)	24	$\Phi_{xx} = -0.021, \ \Phi_{yy} = 0.187, \ \Phi_{xy} = -0.018, \ \Phi_{yz} = -0.193$
5	a(1, 1, 1)	8	$\Phi_{xx} = -0.262,  \Phi_{xy} = -0.120$

the sample undergoes the following transformations: Ce (melt)–(1068 K)  $\rightarrow \delta$ -Ce–(999 K)  $\rightarrow \gamma$ -Ce. Although the  $\delta - \gamma$ transition is well defined (unlike the  $\gamma - \beta$  change), the cooling procedure nevertheless leads to sample contamination by other phases  $(\beta, \alpha)$ . To avoid this, in [82], a single crystal of  $\delta$ -Ce was grown *in situ* (on cooling below 999 K) in an argon atmosphere and its phonon spectrum was then measured by inelastic neutron scattering at T = 1036 K. The dispersal curves of  $\delta$ -Ce were then fitted according to the standard Born-von Kárman force model with five nearest shells (Table 8). As a result, the elastic constants  $c_{11} = 2.20(7)$ ,  $c_{12} = 1.71(8)$ , and  $c_{44} = 1.47(3)$  (in  $10^{10}$  N m<sup>-2</sup> or  $10^{11}$  dyne cm<sup>-2</sup>) were obtained from the direct fitting of the phonon spectrum, or alternatively  $c_{11} = 2.23$ ,  $c_{12} = 1.73$ , and  $\hat{c}_{44} = 1.62$  (in 10<sup>10</sup> N m<sup>-2</sup>, or 10<sup>11</sup> dyne cm<sup>-2</sup>) from the force constants.

The important feature of the phonon spectrum of  $\delta$ -Ce is a pronounced minimum of longitudinal vibrations at  $\xi = 2/3$ (or L2/3) along the  $[\xi, \xi, \xi]$  direction, and also low-lying transverse vibrations along  $T_1[\xi, \xi, 0]$  and  $T_2[\xi, \xi, 2\xi]$ . These anomalies are an indication of the instability toward closedpacked structures (fcc, hcp, and dhcp). In addition, the phonon spectrum is considerably damped, especially at the Brillouin zone boundaries, where its halfwidth is of the same order as the phonon frequency. The large ratio  $A = c_{44}/c' = 5.6$ of two shear constants [see Section 4.1 and Eqn (1)], which is only 2.8 for  $\gamma$ -Ce, implies a large anisotropy of the crystal potential and its instability to tetragonal distortions. The estimated Debye temperature is 95.2 K, and the mean square displacement of a cerium atom is 0.119  $Å^2$ . In general, the phonon spectrum of  $\delta$ -Ce is noticeably softer than in  $\gamma$ -Ce, especially in the frequency range v < 1 Hz, which causes an excess of  $0.45k_{\rm B}$  of lattice entropy per atom. (The total entropy change at the  $\gamma \rightarrow \delta$  transition, including the electronic contribution, is  $0.35k_{\rm B}$ .) Therefore, in contrast to the fcc structure of  $\gamma$ -Ce, the bcc structure of  $\delta$ -Ce is stabilized by the lattice entropy contribution.

We note that lattice properties and the phonon spectrum of  $\delta$ -Ce are very similar to those of the homologue bcc phases of  $\beta$ -Sc and  $\gamma$ -La. Like  $\delta$ -Ce, both  $\beta$ -Sc and  $\gamma$ -La transform into close-packed structures ( $\beta$ -Sc to hcp and  $\gamma$ -La to fcc). As in cerium, the metallic bond in Sc and La is formed by one d- and two s-electrons (see Section 2). This is a further indication that the 4f electrons of cerium do not participate directly in chemical bonding [82] (Section 2).

#### 9. High-pressure phases of cerium ( $\alpha'', \alpha', and \epsilon$ )

#### 9.1 Identification of $\alpha''$ -Ce and $\alpha'$ -Ce

At room temperature and the pressure  $P \approx 5.0-5.5$  GPa, α-Ce transforms into an allotropic modification called  $\alpha'$ -Ce. The identification of the  $\alpha'$  crystal structure became "one of the most controversial subjects concerning highpressure phases" [176]. First,  $\alpha'$ -Ce was considered an fcc structure with a lattice constant that is 4% smaller than in  $\alpha$ -Ce [177]. Then, an hcp structure [178] and finally a C-centered orthorhombic [10] ( $\alpha$ -U) structure (Fig. 14) were reported for  $\alpha'$ -Ce. In a series of X-ray diffraction studies, Zachariasen and Ellinger excluded fcc and hcp as erroneous, but simultaneously found a new cerium phase, which they called  $\alpha''$  [10]. This monoclinic  $\alpha''$ -phase has the I2/m space symmetry (with the lattice constants a = 4.762, b = 3.170,c = 3.169 Å, and  $\beta = 91.73^{\circ}$ ), which can be viewed as a distorted fcc structure. It was first described as a metastable phase: upon pressure release, it transforms into  $\alpha$ -Ce, while on increasing pressure, it becomes  $\alpha'$ -Ce. Next, another monoclinic phase of the C2/m space symmetry was reported [7]. Thus, two  $\alpha''$  phases appear,  $\alpha''$ -Ce(I) and  $\alpha''$ -Ce(II). Later, however, it was demonstrated that both phases are identical and have the same C2/m space symmetry [8]. It has four atoms in the primitive unit cell and can be considered a superstructure formed by doubling the I2/m structure with two atoms in its unit cell (Fig. 15). The problems with the phase identification arose because X-ray patterns were strongly affected by the sample orientation [8].

Thus, it has been established that the sequence of phase transformations in cerium under pressure is as follows:

$$\gamma$$
-Ce (fcc)  $\rightarrow \alpha$ -Ce (cubic)  
 $\rightarrow \alpha'$ -Ce ( $\alpha$ -U) or  $\alpha''$ -Ce ( $C2/m$ )  $\rightarrow \epsilon$ -Ce (bct). (10)

However, it is not clear in this sequence which phase,  $\alpha'$ -Ce ( $\alpha$ -U) or  $\alpha''$ -Ce (C2/m), is stable and which is metastable under pressures from 5 to 12 GPa. This question has been debated for a long time and apparently was closed by the study of McMahon and Nelmes [8].  $\alpha'$ -Ce is slightly denser (0.11(8)%) and the nearest distance between cerium atoms there is 0.1 Å smaller than in  $\alpha''$ -Ce. This indicates that the



**Figure 14.** The base-centered (C) orthorhombic primitive unit cell ( $\alpha'$ -Ce, the *Cmcm* space group, the  $\alpha$ -U structure). It becomes an fcc structure if a = b = c and y = 0.25.



**Figure 15.** The relation between the monoclinic primitive unit cell ( $\alpha''$ -Ce, the *C*2/*m* space symmetry) and the fcc lattice ( $\gamma$ -Ce). (Refs [8, 148].)

 $\alpha$ -U structure should be more favorable energetically than C2/m. However, the  $\alpha$ -U structure is hexagonal-like, the transition to which invokes relatively large displacements accompanied by additional energy losses, whereas the transformation to the monoclinic phase causes only small atomic displacements from the cubic positions. In Ref. [8], the following experiment is described. Starting at room temperature, from almost pure  $\alpha'$ -Ce ( $\alpha$ -U) at P = 7 GPa, the pressure was reduced to 2.5 GPa. When the transformation to the cubic  $\alpha$  phase was complete, the pressure was increased to the initial value (7 GPa). It was then found that the sample was almost entirely in the  $\alpha''$  phase (C2/m).

Glide motions of planes are responsible for other peculiarities of the transformation to  $\alpha'$ -Ce ( $\alpha$ -U). It turned out that the  $\alpha$ -Ce (cubic)  $\rightarrow \alpha'$ -Ce ( $\alpha$ -U) transition proceeds from very few centers of the  $\alpha$  phase, and therefore the phase change apparently depends on grain size. It is also possible that the  $\alpha \rightarrow \alpha'$  transformation requires a minimum critical size of grains. The authors of Ref. [8] pointed out that this observation can explain different branches of the phase sequence, that is, which path,  $\alpha$ -Ce  $\rightarrow \alpha'$ -Ce ( $\alpha$ -U) or  $\alpha$ -Ce  $\rightarrow \alpha''$ -Ce (C2/m), is realized in a cerium sample depends on the method of sample preparation. In 'cold-worked' samples, which were not annealed at high temperature and pressure, the  $\alpha$ -Ce $\rightarrow$  $\alpha''$ -Ce (C2/m) transition occurs. But if the sample is preliminary heated, it supposedly contains nuclei of the  $\alpha'$  phase  $(\alpha$ -U) and transforms into that phase. Interestingly, to some extent, the trend is opposite to that in the  $\gamma \rightarrow \beta$  transition, which is enhanced with as the temperature decreases. McMahon and Nelmes [8] gave convincing arguments that it is  $\alpha''$ -Ce which is thermodynamically stable. The opposite standpoint is represented by the authors of Refs [35, 25]. They argue that if these two phases ( $\alpha'$  and  $\alpha''$ ) coexist at a pressure of 5 GPa, then the  $\alpha''$ -Ce fraction disappears at pressures above 7 GPa, while  $\alpha'$ -Ce is present up to 13 GPa. Other arguments in favor of the metastability of  $\alpha''$ -Ce can be found in [25].

The last transformation in (10) occurs when P > 12 GPa (starting at P = 12.5 GPa and ending at P = 17.7 GPa). The structure and symmetry of  $\varepsilon$ -Ce are well established: it is the body-centered tetragonal lattice [9] with the lattice parameters given in Table 1. However, various phases ( $\alpha$ ,  $\alpha'$ ,  $\alpha''$ , and  $\varepsilon$ ) can be present in a cerium sample in this range of pressures and temperatures, and therefore several phase transformations with a large hysteresis effect are often detected [25]. The complex behavior of such a phase mixture was studied in Ref. [25], with the conclusion that the phase composition depends not only on temperature and pressure but also on the trajectory in the P-T plane leading to a

chosen point of the P-T diagram (the region of phase ambiguity in Fig. 1). Arched phase ( $\alpha$ ,  $\alpha'$ ,  $\alpha''$ , and  $\varepsilon$ ) boundaries were first mentioned in [23].

We also note that based on resistance measurements, the authors of [25] reported the direct transformation from  $\varepsilon$ -Ce to  $\alpha$ -Ce [25]. The transition in the direction  $\alpha \rightarrow \varepsilon$  was established by X-ray diffraction [26]. The slope of the transition boundary between  $\alpha$ -Ce and  $\varepsilon$ -Ce is positive (Fig. 1), but its values in [25] and [26] are quite different.

### 9.2 Condensation schemes of symmetry lowering in high-pressure phases

From the group-theoretical approach, the symmetry lowering from fcc ( $\gamma$ -Ce) to monoclinic  $\alpha''$ -Ce (C2/m) is driven by the condensation of the order parameter at the L point of the Brillouin zone [179]. The corresponding wave vector  $\mathbf{q}_L$  ( $k^9$  in Kovalev's notation [116]) has four rays  $\mathbf{q}_L^i$  (i = 1-4), where each ray is invariant under all symmetry operations of the small group  $\overline{3m}(D_{3d})$ , with the three-fold axis being the main symmetry element. From the basis of the two-dimensional (Eg) representation of the small group (with the basis density functions  $\rho_1^i$  and  $\rho_2^i$ ), we obtain 8 basis functions of the irreducible representation  $L_3^+$  ( $k^9$ ) [115, 116]. As shown in Ref. [148], the condensation of the first function ( $\rho_1^i$ ) of a ray leads to the C2/c space symmetry, while the condensation of the second ( $\rho_1^i$ ) leads to C2/m. Therefore, we obtain the following scheme of condensation to  $\alpha''$ -Ce:

$$Fm3m: L_3^+ |\rho_2(\mathbf{q}_L^1) = \rho| \to C2/m.$$

In general, there are 12 domains of C2/m.

The transformation to  $\alpha'$ -Ce ( $\alpha$ -U) with the *Cmcm* symmetry involves the irreducible representation  $X_5^+$  [115] ( $k^{10}$  in Kovalev's notation [116]) at the X point of the Brillouin zone. In this case, there are three rays (j = 1 - 3), and the small group is  $\bar{4}m(D_{4d})$ . Taking the density components  $\rho_1^j$  and  $\rho_2^j$  as basis functions of the two-dimensional representation ( $E_g$ ), we obtain the six-dimensional irreducible representation  $X_5^+$ . Condensation of three out of its six components gives a cubic symmetry ( $Pn\bar{3}m$  or  $Pa\bar{3}$ ), which is most likely realized in  $\alpha$ -Ce [74] (see Section 6). But if the condensation involves only one component ( $\rho_1^j$  or  $\rho_2^j$ ) of one ray, the symmetry lowers to *Cmcm* (the  $\alpha$ -U structure [5, 6]), which is realized in  $\alpha'$ -Ce:

$$Fm\bar{3}m: \mathbf{X}_{5}^{+}\left[\rho_{1}(\mathbf{q}_{\mathbf{X}}^{1})=\rho\right] \rightarrow Cmcm.$$

This symmetry change results in six different domains. Condensation schemes for cerium phases are summarized in Table 9.

An interesting group-theoretical relation between the space symmetries  $\alpha''$ -Ce (*C*2/*m*) and  $\alpha'$ -Ce (*Cmcm*) is presented in Ref. [180]. The authors propose considering the bcc as a parent structure from which all other phases can be deduced via displacive mechanisms and symmetry lowering. The displacive transformations are divided into two groups: (1) variants of the Burgers mechanism transforming bcc to hcp, dhcp, and 9R structures [181], and (2) variants of the Bain deformations transforming bcc to fcc or bct [182]. The transformation from bcc to the orthorhombic  $\alpha'$  phase ( $\alpha$ -U, or *Cmcm*) is described by a condensation of one out of six components at the N<sub>b</sub> ( $2\pi/a$ )(1/2, 1/2, 0) point of the Brillouin zone of the bcc lattice. The condensation can occur via any component; each of the variants corresponds to one of the six

Phase	Irreducible representation (BZ point) [115]	Number of rays	Number of components of one ray	Qudrupole component symmetry in one ray	Space symmetry
α	$X_5^+$	3	1	$T_{2g}$	$Pn\bar{3}m$ or $Pa\bar{3}$
α′	$X_5^+$	1	1	$T_{2g}$	Стст
α″	$L_3^+$	1	1	$T_{2g}, E_g$	C2/m
3	$X_2^+$	1	1	R <sub>g</sub>	I4/mmm

**Table 9.** Symmetry lowering (order parameter condensation) and space group relations between the (high-symmetry) fcc structure of  $\gamma$ -Ce and low-symmetry phases. 'Rays' and 'components of one ray' here stand for the rays and components of one ray that are involved in the corresponding condensation.

domains. If a Bain deformation is now applied transforming bcc to fcc, then the six formerly equivalent domains become nonequivalent. Some of the domains still correspond to  $\alpha'$ -Ce (with the N point becoming the X point of the Brillouin zone of the fcc lattice), while other domains correspond to the monoclinic  $\alpha''$ -phase (with the N point becoming the L point of the Brillouin zone of the fcc lattice). This mechanism gives a nontrivial group-theoretical relation between  $\alpha'$ -Ce and  $\alpha''$ -Ce and explains the low energy barrier between the two phases.

#### **10.** Conclusions

We have reviewed phase transitions in metallic cerium, taking recent experimental data, including high-pressure measurements, into account [8, 25, 26]. Much attention has been given to the  $\gamma \rightarrow \alpha$  phase transformation with a considerable lattice contribution to the entropy change [27, 80], and novel experimental results [28, 29] (TDPAC spectroscopy) that have revealed a quadrupole electron density component in  $\alpha$ -Ce. This is an unambiguous indication that the  $\gamma \rightarrow \alpha$ transition is a hidden structural transition with space symmetry lowering [73–75].

Experimental data on the epitaxial  $\beta$  phase of Ce grown on niobium surface are also of much interest [171]. On cooling, instead of transforming into  $\alpha$ -Ce, this epitaxial  $\beta$  phase undergoes a transition to a samarium-type crystal structure characteristic of 5d metals. These and other observations suggest that the appearance of the bulk  $\beta$  phase in the P-Tregion between  $\gamma$ -Ce and  $\alpha$ -Ce is caused by specific effects like the large volume change in the  $\gamma \rightarrow \alpha$  transition.

We have also critically discussed recent computational methods and calculations of the  $\gamma \rightarrow \alpha$  phase transition and considered in detail the quadrupole model [74, 37], the peculiarities of the electron structure of atomic cerium, and the simplest chemical bond in the cerium dimer.

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