



## Structural systematics of 4f and 5f elements under pressure

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## Abstract

The present knowledge on the structural systematics of the 4f and 5f elements is reviewed with emphasis on recent new results concerning the structures of the high-pressure phases Sm-V and Nd-IV and the distorted fcc structure typical of all the “regular” 4f and heavier 5f elements at intermediate pressures. Relationships between crystal structures and electronic configurations are discussed also from the point of view of being able to make predictions for new high-pressure phases.

**Keywords:** Systematics; Pressure; Crystal structure; Electronic configurations

## 1. Introduction

When one considers that the structural systematics of lanthanides [1,2] and a comparison of the lanthanide and actinide behaviour under pressure [3] have already been published recently, one could ask whether any further discussion is now justified. However, various new experimental [4–10] and theoretical [11–16] results have added essential new information which casts new light on the earlier results.

What has been discussed in detail in previous papers can be recalled here by the reproduction of the generalized alloy phase diagrams for the lanthanides [3,17–19] and actinides [3–20]. These are shown with some minor revisions in Figs. 1 and 2. With minor modifications for the recent data [4–10], Fig. 1 illustrates the present knowledge about the generalized alloy phase diagram of the lanthanides under ambient conditions. Obviously, there is a common trend at ambient pressure with the structural sequence dhcp → Sm-type → hcp from La to Lu and the reverse trend hcp → Sm-type → dhcp → fcc → distorted fcc under pressure, but with the observation of the fcc phase at ambient temperature and high pressure only up to the element Dy. For Ho, the transition goes directly from dhcp to distorted fcc, and the elements Er, Tm and Lu have not yet been studied up to the pressures where a direct dhcp → distorted fcc transition might be expected at ambient temperature. At elevated temperatures, however, these elements also should first transform into the intermediate fcc structure. Clearly, the elements Yb and Eu at ambient pressure and Ce at moderate pressures show completely different systematics and

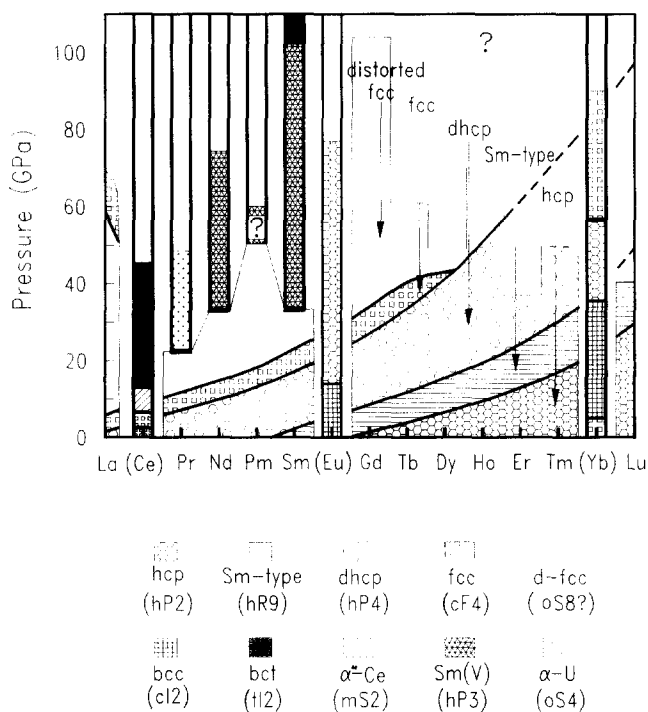


Fig. 1. General diagram for phase relations of lanthanide metals under pressure at ambient temperature, taken from Ref. [3] with modifications for the new results discussed in the text.

with increasing pressure unusual structures have been observed also for Pr, Nd and Sm.

Similar systematics are also presented for the actinides in Fig. 2, with the obvious difference that the anomalies start here for the light elements already at ambient pressures and also the systematics for the heavier actinides are more complicated or less pronounced.

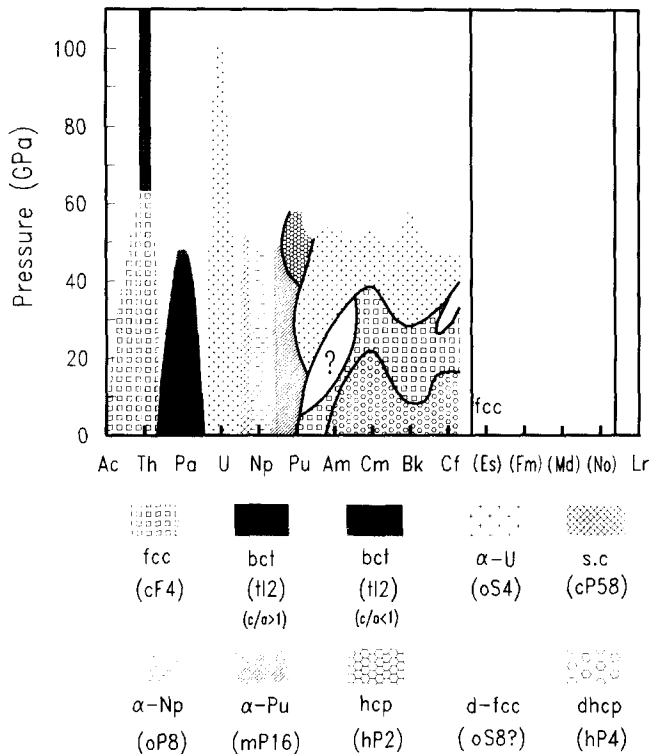


Fig. 2. General diagram for phase relations of actinide metals under pressure at ambient temperature, taken from Ref. [3] with modifications as in Fig. 1.

While the regular systematics had been related primarily to an increase in the d-band occupation under pressure or, in other words, to an  $s \rightarrow d$  transfer under pressure [21,22], all other “anomalies” are commonly attributed to different effects from f electrons.

This paper is devoted primarily to a description of the new features added to these diagrams and to a discussion of these new results from the point of view of new interrelations between these diagrams for the 4f and 5f elements.

## 2. New experimental results

The observation of a new “re-entrant” fcc phase for La under pressures above 60 GPa at room temperature [4] stimulated a more detailed study on the temperature dependence of the phase boundary between the new and old fcc phase with respect to the intersecting “distorted fcc” phase. The result [4] was that the “distorted fcc” phase, La-III, can be considered as a low-temperature phase with a maximum in the phase boundary common to the fcc high-temperature phase (La-II=La-IV) around 30 GPa and 450 K. The observation of the re-entrant stability for the fcc structure in La at higher pressure also fits well to the theoretical prediction [14] that La, in contrast to Th, should remain stable in its fcc structure even when more 4f character is “observed” in band structure calculations for strongly

compressed La in a region where Th transforms to the bct phase [20].

These observations, together with new data and additional considerations on the structure of the “distorted-fcc” phase for Pr under pressure [5], have motivated a more general theoretical and detailed experimental study on the symmetry change at the  $\text{fcc} \rightarrow \text{distorted-fcc}$  phase transition of lanthanides under pressure [8]. Experimental data were taken on La to allow a comparison with the Pr data but to avoid the extra (disturbing) diffraction lines from PrO present in the earlier study [5]. In short, the detailed study [8] on La in the region of the transition from the fcc to the distorted-fcc structure revealed intensity variations for the superlattice reflections, which were very similar to the results for Pr-III, supporting the same structural assignment to both the “distorted-fcc” phases in La and Pr. However, by the use of Landau theory for second-order phase transitions, it was shown that the structure proposed [5] for Pr-III could not evolve by a strictly second-order phase transition from the parent fcc phases La-II, La-IV or Pr-II [8], but some weak first-order character would be required from symmetry considerations whereas the experimental studies give no evidence for the possibly weak first-order character of this phase transition.

Thus, the structure proposed for the distorted-fcc phase of Pr-III [5] with space group  $R\bar{3}m$  and 24 atoms on the positions 6c and 18h in the hexagonal unit cell (in short notation:  $hR24$ ) remains a possible candidate for the La-III phase and also for all the other regular lanthanides. However, there are two more new structures which also fit fairly well to the experimental data, and only one of them allows for a true second-order phase transitions [8]. This structure [8] has the space group  $Cmmm$  with eight atoms in the orthorhombic unit cell at the positions 4g and 4j and can be denoted oS8. A detailed evaluation of the intensity variations reveals that the intensity of the observation superlattice reflections fits, however, slightly better to  $hR24$ . As long as there is no indication of a weak first-order character of this transition, one has to take into account the possible assignment of oS8 to the “distorted-fcc” structure.

The stability of the Pr-III phase with respect to the next phase, Pr-IV, has been studied recently by energy-dispersive X-ray diffraction experiments in the pressure region of 20 GPa at elevated temperatures [9]. The triple point between Pr-II, -III and -IV was located around 500 K and 21 GPa. Owing to the second order-character of the II–III phase transition, the slope for the II–IV phase transition could also be estimated close to the triple point, but further measurements are desirable for an extension of this phase diagram into the higher temperature region.

Another long-standing problem that has been solved recently [7] concerns the “low-symmetry” phases [3,23–25] Sm-V and Nd-IV, which were not considered by other authors [10,26,27].

Fig. 3 illustrates most clearly that high-resolution energy-dispersive X-ray diffraction data [7] give clear fingerprints for distinction between the patterns of Sm-IV and Sm-V phases. The assignment in Fig. 3 together with the intensity data allow for an unambiguous structure determination [7] for Sm-V and results in the two enantiomorphous space groups  $P3_121$  and  $P3_221$  with three atoms on the 3a positions, which are the same as for trigonal Se and Te with the same short notation  $hP3$ , but the different values for the atomic position parameters result in a structure with open channels instead of helical chains, reflecting only a slight distortion with respect to a fcc parent phase. In fact, this assignment is compatible also with all the previous lower resolution X-ray data for the same phases and leads to the speculation that the poorer resolution in the earlier study on Pm up to 60 GPa [25] may have missed the observation of the transition into this Sm-V-type structure. Finally, the analysis of the pressure–volume data for the Sm-V phase gave evidence [7] for 4f bonding contributions in this phase, which would make this new prototype structure a good candidate also for other 4f and 5f elements on the borderline for the onset of f-

electron bonding. Thus, one can speculate whether this  $hR3$  structure should not also occur at other places in Figs. 1 and 2, probably covering the region between Nd-IV and Sm-V, with a chance of the occurrence of this structure also in Pr above 50 GPa and in the heavier lanthanides at higher pressures. Also, a new evaluation of earlier data for the heavier actinides may be considered from this point of view.

### 3. New theoretical aspects

Much progress has been made in detailed total energy calculations not only for Th and La [14–16] but also for Sm [11], revealing the essential contribution of f-electron character in the band for stability of the bct structure (Pearson notation:  $tI4$ ). More general considerations on reconstructive transformations in actinide elements [12,13] point to the fact that a generalization of Landau’s theory of phase transitions can give valuable hints about the different mechanisms acting in these phase transitions, and one can expect that both the 4f and 5f elements under pressure may provide the necessary data to develop these ideas in more detail.

### 4. Conclusions

The new experimental data and theoretical calculations for 4f elements under pressure also give new stimulation for further studies on the phase diagrams of both 4f and 5f elements. In fact, many questions may still be hidden behind the white areas in Figs. 1 and 2, as illustrated by these new results on the borderlines of these areas.

Finally, new concepts from the point of view of the different transformation mechanisms may be a new area for further studies in the near future.

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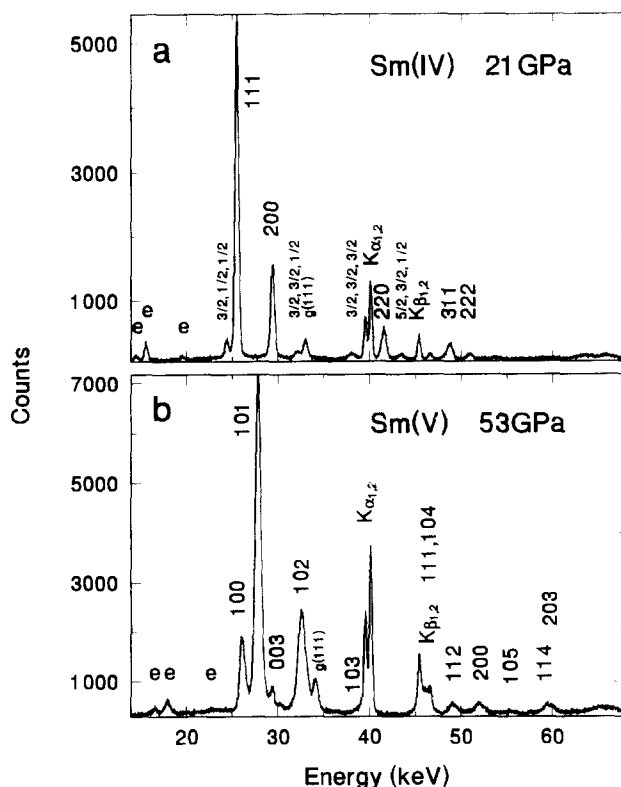


Fig. 3. Energy-dispersive X-ray diffraction spectra for Sm-IV and Sm-V phases, taken from Ref. [7] with the assignment according to the new structural models [7,8].

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