Theoretical high-pressure studies of Cs metal

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We have studied the crystal structures of cesium metal under high compressions by means of first-principles self-consistent total-energy calculations within the local-density approximation using the full-potential linear-muffin-tin-orbital (FPLMTO) method. Our results confirm the recent high pressure experimental observations of crystallographic phase transformations in Cs [Schwarz *et al.*, Phys. Rev. Lett. **81**, 2711 (1998)]. The calculated transition pressures agree well with the measured data. Also the computed axial c/a ratio for Cs-IV and Cs-VI is found to be in good agreement with experiment. Similarly the calculated a/b, c/b ratios as well as the three internal parameters for the Cs-V phase agrees very well with measurement. The structural stability of different phases in Cs is also supported by canonical d-band model calculations.

In textbooks on solid state physics alkali metals are often used as examples of so-called simple metals, where the electronic structure to a large extent can be compared with the highly simplified electron gas model. However, they are also of technological interest primarily as liquid coolants for nuclear reactors. These metals have high compressibilities and low melting points so their phase diagrams have been determined over a considerable range of volume compressions. Unexpectedly, these high pressure studies show complex phase diagram with many crystal structures. Cs is the most studied alkali metal and exhibits an unusual sequence of phase transitions under pressure. Cs is also the only alkali metal which has been demonstrated to become superconducting under high pressure.[1] At ambient conditions, Cs is stable in the high symmetry bcc structure at ambient conditions. It transform to a fcc phase at 2.3 GPa[2,3] and at 4.2 GPa it shows an isostructural transition with a 9% volume collapse.[2] At around 4.3 GPa, the fcc phase transforms to a tetragonal structure (Cs-IV) which is stable up to 10 GPa,[4] where it undergoes a new transformation to a new structure (Cs-V). Very recently Schwarz *et al.*[5] have solved the long standing problem of the structure of the high pressure Cs-V phase. It has an orthorhombic structure with space group Cmca and the unit cell contains 16 atoms. This structure is not unique for Cs but has also recently been found by Hanfland *et al.*[6] for Si. The Cs-V phase is stable up to 72 GPa, where Takemura *et al.*[7] have observed a new high pressure modification at 72 GPa. The crystal structure of this new phase is the hexagonal close packed (hcp) or double hexagonal close packed (dhcp) structure, which is stable up to the highest studied pressure of 92 GPa.

At ambient conditions the regularities of the crystal structures across the d transition series (close packed—fcc and hcp, or rather close packed—bcc) as well as within the lanthanide series, are well known to be governed by the d-electron behavior.[8,9] To a large extent this picture also explains the crystallographic properties observed at high compressions for these elements. The elegant and simple explanation presented in Refs. 8 and 9, has proved to be very useful in more recent studies of the crystal structure stabilities in these materials. For instance, an increase of the d occupation of a certain metal is expected to modify the crys-

tal structure. Such an increase can be achieved by compression. As a matter of fact a large number of high pressure investigations have been performed and indeed crystallographic phase transitions have been found for many systems. Most of these experimental studies can be explained on the basis of the work by Duthie and Pettifor[8] and Skriver.[9] McMahan[10] has performed LMTO-ASA calculations for Cs, Rb, and K and investigated the high pressure structures above the so-called s-d transition. McMahan has shown that at very high pressure Cs transforms to the hcp structure.

The main aim of the present contribution is to investigate theoretically the stability of the different phases in Cs metal using very accurate total energy calculations as well support these calculations using a simple model based on canonical band theory. Thereby, we will be able to present independent evidence for the correctness of the crystal structure assignment of the Cs-V phase. In view of the difficulties which have been attached to this structure determination, this is of considerable interest.

In order to study the electronic structure and derive the total energy of Cs, we have used the full-potential linear muffin-tin-orbital (FPLMTO) method.[11] The calculations were based on the local-density approximation and we used the Hedin-Lundqvist[12] parametrization for the exchange and correlation potential. Basis functions, electron densities, and potentials were calculated without any geometrical approximation.[11] These quantities were expanded in combinations of spherical harmonic functions (with a cutoff $l_{max} = 8$) inside nonoverlapping spheres surrounding the atomic sites (muffin-tin spheres) and in a Fourier series in the interstitial region. The muffin-tin sphere occupied approximately 50% of the unit cell. The radial basis functions within the muffin-tin spheres are linear combinations of radial wave functions and their energy derivatives, computed at energies appropriate to their site, principal as well as orbital atomic quantum numbers, whereas outside the muffin-tin spheres the basis functions are combinations of Neuman or Hankel functions.[13,14] In the calculations reported here, we made use of pseudo-core $5s$, $5p$ and valence band $6s$, $6p$, and $5d$ basis functions for Cs with corresponding two sets of energy parameters, one appropriate for the semicore $5s$ and $5p$ states, and the other appropriate for the valence states. The
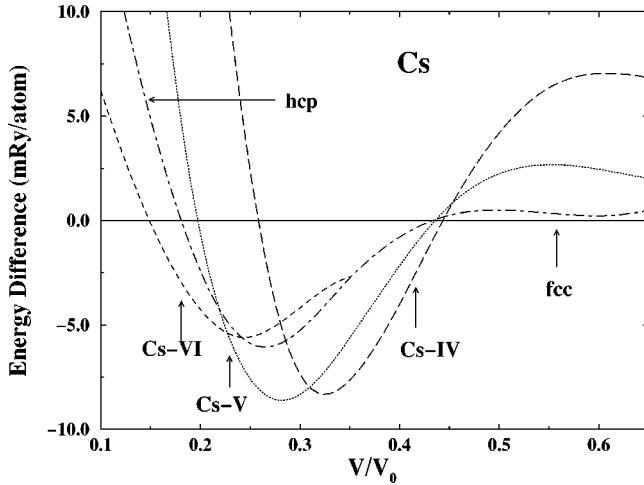
FIG. 1. Energy difference between the fcc, Cs-IV, Cs-V, Cs-VI and hcp crystal structures for Cs as a function of volume (V/V_0, V_0=experimental equilibrium volume). The fcc structure is used as the zero energy reference level.

resulting basis formed a single, fully hybridizing basis set. This approach has previously proven to give a well converged basis.[11] For sampling the irreducible wedge of the Brillouin zone, we used the special k-point method.[15] For fcc, Cs-IV, Cs-V, Cs-VI, and hcp phases we have used 60, 87, 68, 65, and 60 k points in IBZ, respectively. We have checked the convergence of the total energy with respect to the number of k points. The total energies are converged within 0.1 mRy.

In Fig. 1 we show the total energy difference between pertinent crystallographic structures for Cs as a function of volume. Here we compare the fcc, Cs-IV, Cs-V, Cs-VI and hcp phases, where the energy of the fcc structure is taken as the reference level. It is most satisfying to notice that our calculations reproduce the observed crystal structure sequence; fcc→Cs-IV→Cs-V→Cs-VI with increasing pressure. Our calculated transition pressure for fcc→Cs-IV is 5.0 GPa, close to the experimental value of 4.3 GPa.[4] Further compression leads to the transition between the Cs-IV and Cs-V structures. Experimentally this transition takes place at about 10 GPa.[5] Our theoretical value for the critical pressure is 13 GPa, again in good agreement with the experimental data. At even higher compressions, the hcp structure is found to become the stable phase. Our calculated transition pres-

TABLE I. Calculated and experimental transition pressure (GPa).

	Transition pressure	
	Expt.	Calc.
fcc→Cs-IV	4.3 [a]	5.0
Cs-IV→Cs-V	10.0 [b]	11.0
Cs-V→Cs-VI	72.0 [c]	56.0

[a]Takemura et al. (Ref. 4).
[b]Schwarz et al. (Ref. 5).
[c]Takemura et al. (Ref. 7).

TABLE II. Calculated and experimental lattice and internal parameters for Cs-V phase.

	Calc.	Expt. [a]
$y(8f)$	0.175	0.1729
$z(8f)$	0.331	0.327
$x(8d)$	0.217	0.216
a/b	1.680	1.691
c/b	0.985	0.995

[a]Schwarz et al. (Ref. 5).

sure of 56 GPa is in fair agreement with the experimental value of 72 GPa.[7] Our calculated transition pressures along with experimental data are shown in Table I.

In Table II we show our calculated relaxed axial ratio and positional parameters for the Cs-V phase. These theoretical data are in good agreement with the experiments. We have also compared our calculated c/a for the tetragonal (Cs-IV) and double hexagonal phase (Cs-VI) with the experimental c/a. This is shown in Table III and again the agreement between experiment and theory is very good.

In order to study the one-electron contribution to the stabilization of the different structures we proceed with an analysis which has previously been made for the hcp, fcc, and bcc structure stabilities of the transition metals. Namely, we study the canonical d bands for the presently investigated structures. The canonical bands which are a conceptual backbone of the LMTO method, have volume and energy independent structure constants as important ingredients. However, a straightforward application of canonical bands is not successful in the description of complex structural phase transitions (comparing fcc, bcc, and hcp of course works very well). By adopting the structural energy difference theorem[8] it may however be possible to describe such trends. Hence we have scaled the canonical bands of each structure so that they give the same second moment (i.e., have the same overlap repulsion) and then we have calculated the eigenvalue sum. This is analogous to the structural energy difference theorem and identifies one single mechanism that is the driving force for the structural transitions in Cs. We display in Fig. 2 the canonical energy difference for the three structures with respect to the fcc structure as a function of the d band-filling. Notice that for d band-fillings of up to 0.4 the eigenvalue sum of the canonical bands stabilizes the fcc structure, for d band-filling between 0.4 to 0.55, it stabilizes Cs-IV, for 0.55 to 0.8, it stabilizes Cs-V and beyond 0.8 and up to 2.0 it shows the stability of hcp or dhcp (Cs-VI) phase.

TABLE III. Calculated and experimental c/a ratio for tetragonal (Cs-IV) and $c/2a$ for double hexagonal close packed (Cs-VI) phases.

	Calc.	Expt.
Cs-IV	3.73	3.729 [a]
Cs-VI	1.63	1.612 [b]

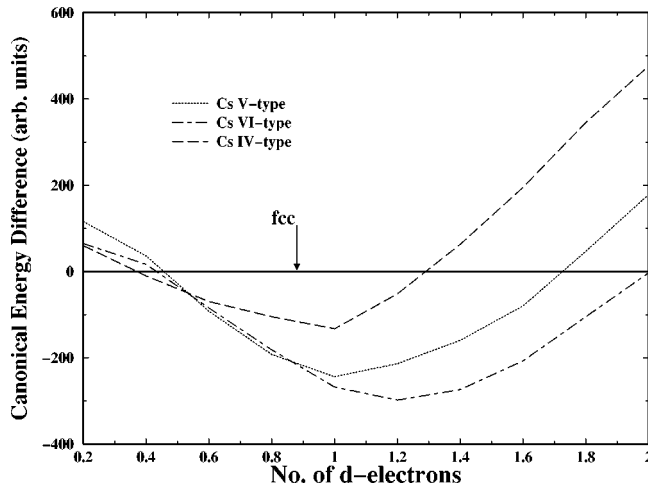[a]Takemura et al. (Ref. 4).
[b]Takemura et al. (Ref. 7).

FIG. 2. Energy differences obtained from canonical d bands as a function of the d band filling for Cs-VI (dotted-dashed), Cs-IV (long dashed), and Cs-V (dotted line) structure. The fcc (solid line) phase is used as the reference level, and is set equal to zero.

Hence, the structural sequence in Cs metal under pressure can be understood as follows: at ambient conditions the d bands are almost empty and when we apply pressure, we start to fill d bands due to a transfer of s electrons in to predominantly d-bands. Once the s to d transition is completed, i.e., the $6s$ electron states is completely transformed to the d band, the hcp structure becomes stable. From the periodic table one also notices that for a metal (yttrium) with one d electron, the hcp phase is stable. The canonical one electron energies in Fig. 2 suggests that the Cs-V phase can be stabilized also for other metals which have a number of d electrons between 0.55 to 0.8, e.g., formed by alloying.

In summary we have shown that modern electronic structure theory is sufficiently refined to give an accurate description of the newly discovered high pressure behavior of Cs. This suggests that the local density approximation (LDA) based on the FPLMTO method can be used to search for the Cs-V type phase in other alkali metals. Further, our simple model calculations based on canonical d bands reproduce the structural phase transition in Cs metal. This is rather interesting since it identifies one term as the driving force for the observed structural transitions in Cs, i.e., the binding due to the d-band formation and the accompanying overlap repulsion. All other terms in the LDA (or GGA) total energy expression are of less importance for driving the structural transitions in Cs, and in order to understand high pressure experiments in general it is valuable to identify one or a few terms as being the most important ones for determining structural phase transitions. Our model calculations also suggest that the Cs-V phase can be stabilized in the other alkali metals which have d electrons in between 0.55 to 0.8, provided that the one electron eigenvalues play the dominant role for the stability of the different structures.

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