

## Theoretical high-pressure studies of caesium hydride

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## LETTER TO THE EDITOR

**Theoretical high-pressure studies of caesium hydride**R Ahuja<sup>†</sup>, O Eriksson<sup>†</sup>, J M Wills<sup>‡</sup> and B Johansson<sup>†</sup><sup>†</sup> Condensed Matter Theory Group, Department of Physics, Uppsala University, BOX 530, S-751 21, Uppsala, Sweden<sup>‡</sup> Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

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**Abstract.** We have investigated the alkali hydrides theoretically 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 CsH (Ghandehari K, Luo H, Ruoff A L, Trail S S and DiSalvo F J 1995 *Phys. Rev. Lett.* **74** 2264). The calculated transition pressures for the occurrence of the CsCl and CrB crystal structures as well as the associated theoretical volume changes agree with the experimental data. We also predict a similar high-pressure behaviour for RbH and KH but not for NaH and LiH.

The behaviour of hydrogen at high pressure is central to a number of fundamental problems in condensed matter and planetary science [1]. For example, the possibility of the formation of a proton hydride at high pressure has recently been raised [2]. Also the metal–hydrogen systems have received wide attention partly due to the large number of technical applications [3]. Among the different classes of hydrogen compounds the alkali and alkaline-earth metals form so-called ionic hydrides. In these systems hydrogen may be considered as the first member of the halogen group of elements and formally it behaves as an  $H^-$  ion. Support for this view can be obtained from the observed crystal structures of these compounds which are typical for ionic systems (NaCl and CsCl). However, as described below, the chemical bonding of these systems changes drastically under compression with corresponding crystallographic phase transitions. In comparison to the alkali halides, the hydrides show similar structural behaviour, both at equilibrium and at elevated pressures, although they are somewhat less ionic. It is particularly useful to recall that the heaviest alkali halide, caesium iodide (CsI), has been studied very extensively both experimentally and theoretically [4–6] and that under pressure CsI undergoes a structural sequence  $CsCl \rightarrow$  orthorhombic structure (space group  $Pm2m$ )  $\rightarrow$  hexagonal, illustrating the above-mentioned change in the nature of the chemical bonding under compression.

Very recently Ghandehari *et al* [7] performed most interesting high-pressure experiments for CsH using energy-dispersive x-ray diffraction (EDXD) with synchrotron radiation. Their main new result is the observation of a new orthorhombic high-pressure phase at 17.5 GPa. They identified this high-pressure phase as the chromium boride structure, CrB, with the  $Cmcm$  space group. At low pressures, their observed transition pressure for the  $NaCl \rightarrow CsCl$  structure is 0.83 GPa which is consistent with earlier measurements by Hochheimer *et al* [8] and Bashkin *et al* [9]. The main aim of the present letter is to use the new experimental findings of the orthorhombic phase in CsH as a sensitive test of the accuracy of the theoretical description of the electronic structure of a hydride system. This

aspect has come very much in focus recently, due to the serious difficulties one encounters in the understanding of the electronic structure of  $\text{YH}_3$ . It is claimed that standard local-density theory [10] (LDA) is insufficient for a proper description of the hydrogen-derived states in this trihydride [11, 12]. Since the different crystal structures of CsH are associated with different degrees of ionicity, the correctness of the LDA treatment of the H states is likely to vary with structure. Such variations of the error would affect the energy comparisons between the different phases considerably. An additional motivation for the present work is that one would like to have evidence of the nature of the driving force behind the occurrence of the observed structural sequence.

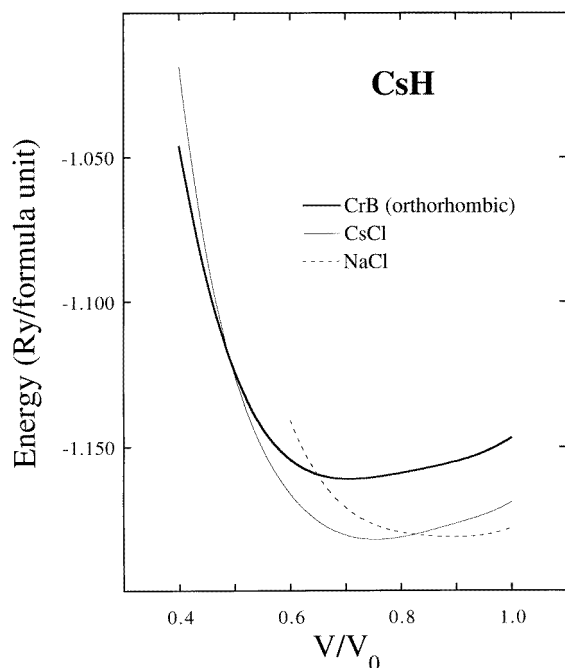
In order to study the electronic structure of CsH we have used the full-potential linear-muffin-tin-orbital (FPLMTO) method [13]. The calculations were based on the local-density approximation and we used the Hedin–Lundqvist [14] parametrization for the exchange and correlation potential. Basis functions, electron densities, and potentials were calculated without any geometrical approximation [13]. These quantities were expanded in combinations of spherical harmonic functions (with a cut-off  $\ell_{max} = 8$ ) inside non-overlapping 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, and principal as well as orbital atomic quantum numbers, whereas outside the muffin-tin spheres the basis functions are combinations of Neuman or Hankel functions [15, 16]. In the calculations reported here, we made use of pseudo-core 5s, 5p and valence band 6s, 6p and 5d basis functions with two corresponding sets of energy parameters, one appropriate for the semi-core 5s and 5p states, and the other appropriate for the valence states. The resulting basis formed a single, fully hybridizing basis set. This approach has previously proven to give a well converged basis [13]. For sampling the irreducible wedge of the Brillouin zone we used the special- $k$ -point method [17]. In order to speed up the convergence we have associated each calculated eigenvalue with a Gaussian broadening of width 20 mRyd.

**Table 1.** Calculated lattice and internal parameters at two different volumes for CsH. Note that the experimental values are for CrB at equilibrium not for CsH.

	$V/V_0 = 0.40$	$V/V_0 = 0.50$	Experimental <sup>a</sup>
$u(\text{Cs})$	0.140	0.139	0.146, 0.143
$u(\text{H})$	0.428	0.422	0.440, 0.430
$b/a$	2.68	2.67	2.65
$c/a$	1.07	1.07	0.99

<sup>a</sup> Wyckoff [18].

At high pressure the newly determined crystal geometry of CsH is the orthorhombic CrB structure. CsH in the CrB structure has the Cs atom at the Cr position and the H atom at the B position. In this structure Cr and B take the 4c positions:  $\pm(0.0, u, 0.25; 0.50, u + 0.50, 0.25)$  [18]. In the initial calculations we chose the same relative internal positions for Cs and H as Cr and B have in CrB at ambient conditions. Thus we set the values of  $u(\text{Cs})$  and  $u(\text{H})$  equal to 0.146 and 0.440, respectively. Further, we have initially taken the same value for the axis ratios,  $b/a$  and  $c/a$ , as observed for CrB, i.e., 2.647 and 0.988, respectively. After this we varied each of the free parameters  $u(\text{Cs})$ ,  $u(\text{H})$ ,  $b/a$  and  $c/a$  separately. The minimized structural parameters were found to be weakly dependent on volume, and are listed in table 1.



**Figure 1.** The total energy for CsH as a function of volume for three different crystal structures: NaCl, CsCl and CrB.  $V_0$  is the experimental equilibrium volume for the NaCl structure.

In figure 1 we show the calculated total energy of CsH as a function of volume for the CrB, CsCl and NaCl structures. Notice that the theoretical equilibrium volume is largest for the NaCl structure and smallest for the CrB structure. This finding is directly consistent with the fact that the packing is more open for the NaCl structure and more closed packed for the CrB structure. If the chemical bonding is assumed to be dominated by two terms, an attractive bonding (Madelung) contribution and a repulsive Born–Mayer energy (as was done previously for the alkali halides [19, 20]), this trend in packing then follows. The reason for this is that with decreasing volumes the repulsive Born–Mayer contribution will dominate and favour the structure with the best packing, i.e., in the present case the CrB structure.

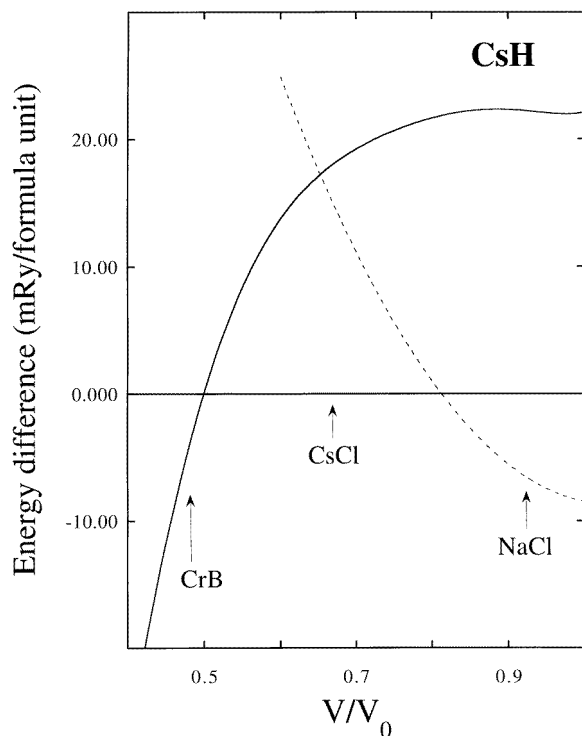
**Table 2.** Calculated and experimental transition pressures (GPa) and volume changes (%).

	Transition pressure		Volume change	
	Experimental <sup>a</sup>	Calculated	Experimental <sup>a</sup>	Calculated
NaCl → CsCl	0.83	0.80	8.4	12.5
CsCl → CrB	17.5	17.6 (22.0 <sup>b</sup> )	6.3	10.0 (6.6 <sup>b</sup> )

<sup>a</sup> Ghandehari *et al* [7].

<sup>b</sup> With unoptimized parameters; i.e. the values observed for CrB.

As a function of volume we show in figure 2 the total-energy difference between the three different crystal structures observed for CsH, where the energy of the CsCl structure is taken as the reference level. As can be seen, the NaCl structure is stable at the experimental volume



**Figure 2.** The energy difference between the NaCl, CsCl and CrB crystal structures for CsH as a function of volume ( $V/V_0$ ,  $V_0$  = experimental equilibrium volume). The CsCl structure is used as the zero-energy reference level.

( $V/V_0 = 1.0$ ) in agreement with crystal data. Under compression, the calculations show that CsH first undergoes a structural phase transition from NaCl to CsCl. The calculated pressure for this transition is 0.80 GPa, which should be compared with the experimental value of 0.83 GPa [7]. After this crystallographic change the CsCl phase is stable for a quite large range of volumes, but when  $V/V_0 = 0.5$  the CsCl phase is calculated to transform to the orthorhombic (CrB) phase. The theoretical pressure for this transition is 17.6 GPa, to be compared with the experimental value of 17.5 GPa. The experimental volume of the CsCl structure at the transition is  $V/V_0 = 0.53$ . The calculated and experimental transition pressures are also collected in table 2. The crystallographic behaviour obtained from our full-potential calculations, shown in figure 2, is thus in very good agreement with experiment. It is also consistent with the above-mentioned, simple model for the chemical bonding. As already mentioned, at the lowest volumes the structure with a better packing is stable, due to the repulsive Born–Mayer energy.

In figure 3 we show the experimental equation of state and compare our calculated transition pressures and volume changes with experiment. Note that the experimental and theoretical results agree very well in absolute numbers. At the highest compression (not shown in figure),  $V/V_0 = 0.26$ , the experimental pressure is 253 GPa. The corresponding theoretical pressure for this volume compression is 260 GPa which is indeed a most satisfying agreement. Thus, since also the calculated transition pressure for the CsCl  $\rightarrow$  CrB phase transition agrees well with experiment, this directly implies that the volume change associated with the crystallographic rearrangement is also well reproduced by theory.

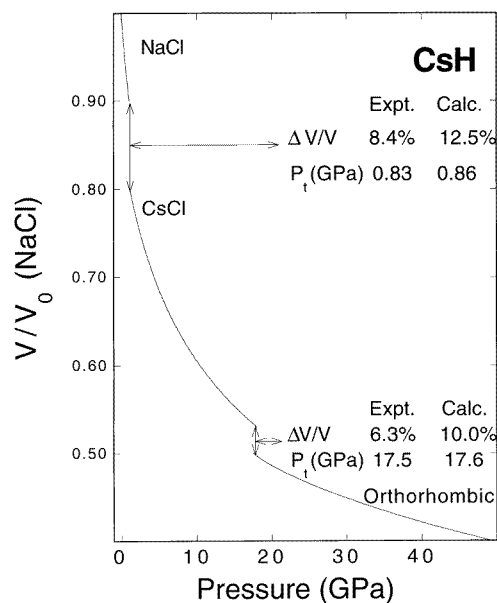


Figure 3. The experimental pressure–volume relation for CsH.

In order to understand the stability of the different structures, we have to consider the different contributions to the total energy. In an ionic system the attractive Madelung potential favours a low number of nearest neighbours for a given volume. Similarly, the one-electron-band energy also tends to favour more open structures. Turning now to the coordination number of CsH, we first notice that the NaCl phase has coordination number 6 whereas the CsCl structure has coordination number 8. In the CrB structure, both the anion and cation atoms have higher coordination number than in the CsCl structure [21, 22]. At large volumes the band and Madelung terms dominate the total energies, so the lowest-energy structure is clearly the NaCl structure. However, as the volume decreases the repulsive Born–Mayer term becomes more dominant, and when sufficiently compressed the lowest-energy phase becomes a structure like CsCl or CrB. Thus with increasing pressure CsH shows an increase in the number of nearest neighbours (n.n.); starting from 6 n.n. (NaCl), via a structure with 8 n.n. (CsCl), into a phase with more than 8 n.n. (CrB). This is consistent with conventional expectations when the pressure is increased. It is explained by the fact that at the equilibrium volume the Madelung energy gives the dominant contribution to the total energy. With compression, the core repulsions become of much larger significance and eventually they dominate and give rise to more efficiently packed structures.

In summary we have shown that modern electronic structure theory is sufficiently accurate to properly describe the newly discovered high-pressure behaviour of CsH. We found no evidence implying that the local-density approximation is inappropriate for the hydrogen states in this particular compound. It now becomes of interest to ask whether it is possible also to stabilize other alkali hydrides in the CrB structure, provided that the external conditions are appropriately adjusted. To answer this question we compared the CrB phase with the NaCl and CsCl structures for RbH, KH, NaH and LiH. First of all we found that all of these alkali hydrides show a phase transition from NaCl  $\rightarrow$  CsCl structure.

We also found a phase transition from CsCl  $\rightarrow$  CrB structure in RbH and KH. However, for NaH and LiH we have not found the CrB phase down to the reduced volumes ( $V/V_0$ ) 0.20 and 0.15, respectively. The reason for this is the absence of nearby d states, and therefore there is no d-s hybridization influencing the valence band states. Accordingly there is no effective occupation of d states which would lead to the favouring of a distorted structure like CrB through the band energy. For RbH and KH, the CrB phase is predicted to appear at the reduced volumes 0.30 and 0.25, respectively, and the corresponding pressures are calculated to be 35.0 GPa and 176.0 GPa, which today can be reached in the laboratory. Thus we predict that RbH and KH will transform to the CrB phase at high pressures and we welcome experimental work investigating our predictions.

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