# New High Pressure Crystal Structure and Equation of State of Cesium Hydride to 253 GPa

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A new orthorhombic high pressure phase was observed in CsH at approximately 17.5 GPa and $V/V_0 = 0.53$. This high pressure phase was assigned to the CrB structure with the *Cmcm* space group based upon 19 x-ray diffraction peaks. It was studied to $V/V_0 = 0.260$ at 253 GPa. This is the highest compression measured in the ionic alkali hydrides to date. At 253 GPa, the bulk modulus of CsH (881 GPa) is nearly double that of diamond at atmospheric pressure (442 GPa).

In metallic hydrides the hydrogen particle forms both covalent and ionic bonds. At ambient pressure, transition metal hydrides have covalent bonding, whereas alkali metal hydrides are principally ionic [1]. The alkali halides are assumed to have a complete charge transfer of $1.0e$ between alkali anions and halide cations. By comparison, the alkali hydrides are computed to have a charge transfer of $0.73e$ [2]. While more covalent than the alkali halides, the alkali hydrides are crystallographically similar to the alkali halides and are expected to behave similarly with the increasing pressure.

While we commonly think of the alkali hydrides as ranging from LiH to CsH, there is the interesting possibility that the hydrogen may, at high pressure, form proton hydride. At atmospheric pressure hydrogen forms a molecular solid with covalent bonding. The sum of the ionic radii for the hydrogen anion and cation are much greater than the radius of the covalent molecule. However, it has been shown that the ionic radii are highly pressure dependent [1], so that at high pressures the formation of a stable ionic-bonded solid may be possible if the sum of the ionic radii becomes less than the radius of the covalent molecule at that pressure. The formation of the proton hydride [3] by ionic bonding at elevated pressures could be a precursor to metallic hydrogen in the following transition steps: $H_2 \rightarrow [H^+ H^-] \rightarrow 2H^+ + 2e$. This may substantially increase the transition pressure to metallic hydrogen currently computed to be 300 to 350 GPa [4,5]. The alkali metal hydrides $[M_1^+ H^-]$ are analogous to the proposed ionic hydrogen hydride, and studies of the alkali hydrides may shed light upon the behavior of hydrogen and its possible transition to a metallic state.

The alkali hydrides have the interesting property that the reduced mass for the $M$H pair is nearly equal to the mass of the hydrogen atom, whereas for CsI, the reduced mass is 64.72 times that of the hydrogen atom. Also, at megabar pressures the material is many times stiffer than at atmospheric pressure. For these reasons, the phonon peaks of the alkali hydrides at megabar pressures are expected to be in the $1-2$ $\mu$m range rather than the

$50-100$ $\mu$m range of the alkali halides at atmospheric pressure.

At ambient pressure, the alkali hydrides have the NaCl $B1$ structure and, with the exception of LiH, have been observed to transform to the CsCl $B2$ structure at elevated pressures [2,6,7]. Their counterparts, the alkali halides, crystallize into the NaCl $B1$ structure or the CsCl $B2$ structure at room pressure. CsI with the $B2$ structure at ambient conditions transforms from $B2$ to orthorhombic (*Pm2m*) [8]. NaI and NaBr with the $B1$ structure at ambient conditions undergo the phase sequence of $B1$ to orthorhombic (GeS), as observed by Yagi, Suzuki, and Akimoto [9]. We observed an orthorhombic high pressure phase for CsH beginning at approximately 17 GPa, which we followed to 253 GPa.

Single crystals of CsH for synchrotron diffraction studies were prepared from the reaction of Cs (99.98%, Johnson Matthey) and $H_2$ (99.9995%, Matheson) in a Rene alloy autoclave. Because of the extreme reactivity of the Cs and CsH, all manipulations were carried out in an argon drybox. The Cs was heated to 625 °C for 30 h under a hydrogen overpressure of 300 atm and condensed onto a silver or stainless steel cold finger at 200 °C to form CsH. The colorless, transparent crystals were cubic in habit and ranged from single crystals 2 mm in size to polycrystalline fragments. The sample, which was a single phase of polycrystalline material, was studied by x-ray powder diffraction and had a lattice parameter of 6.388(1) Å which is consistent with the value reported in the literature [10]. For the high pressure studies, the sample was loaded into the diamond anvil cell in the drybox using a microscope with a video camera. No pressure medium was used.

Four experiments were performed using energy dispersive x-ray diffraction (EDXD) with synchrotron radiation to collect structural data for CsH. One used ruby fluoresence as a pressure scale [11] to 37 GPa and employed type Ia diamond anvils with 600 $\mu$m diameter flat culets with a sample chamber initially at 250 $\mu$m in diameter and 100 $\mu$m thick. The second experiment employed

       

molybdenum [12] as a pressure marker to 58 GPa and was performed using type IIa diamond anvils with 300 $\mu$m flat culets with a sample chamber 75 $\mu$m in diameter and 40 $\mu$m thick initially. The third experiment was done using platinum [13] as a pressure marker to 253 GPa and type Ia beveled culet diamonds with 75 $\mu$m tips beveled at 8° to a diameter of 350 $\mu$m. The initial sample chamber was 50 $\mu$m in diameter and 35 $\mu$m thick. The fourth experiment was performed in a cell similar to that used in the first experiment. Two angles were used to collect EDXD spectra of orhtorhombic CsH at the same pressure of 25.1 GPa as measured by ruby fluorescence.

Figure 1 shows typical diffraction patterns collected in the first experiment for CsH in three phases. The patterns here for CsH are (A) the $B1$ NaCl phase at 0.14 GPa, (B) the $B2$ phase at 3.7 GPa, and (C) the new orthorhombic high pressure phase at 22.6 GPa. The data fitted an orthorhombic cell with four atom pairs and a 6.3% volume decrease from the $B2$ phase at an average transition pressure of 17.5 GPa.

Figure 2 shows the data of the fourth experiment performed at 25.1 GPa taken with two different diffraction angles corresponding to $Ed = 41.301$ and 78.396 keV Å. A portion of the low angle data is given in the inset of Figure 2. This shows the (020) peak with a relative intensity of 3.7%. At $Ed = 41.301$ keV Å, this peak could not be observed because of strong x-ray absorption in the diamond at the expected energy of 8.682 keV. The main portion of Figure 2 shows the data
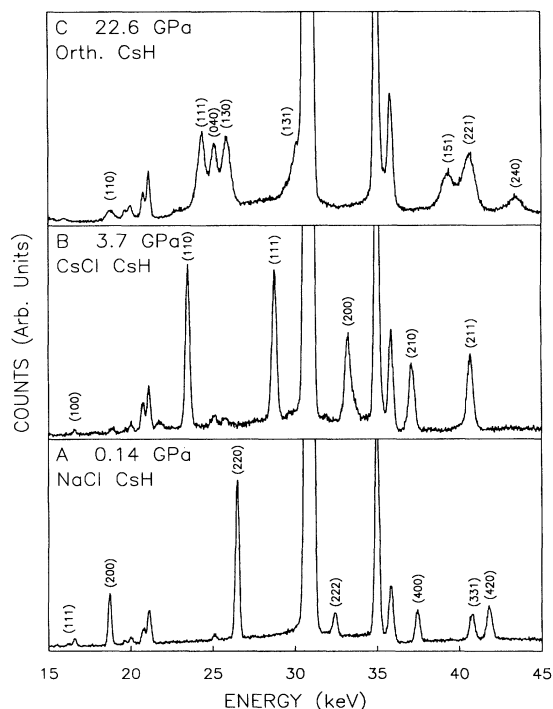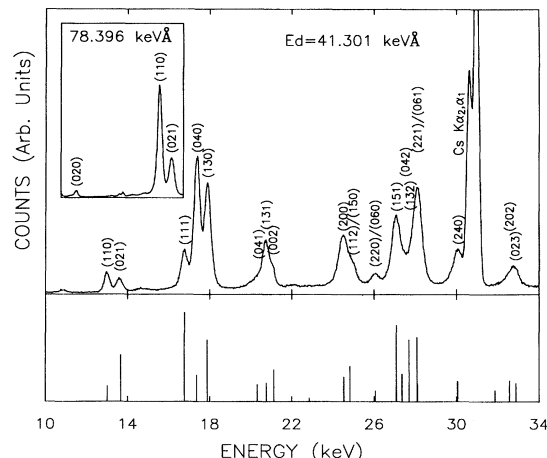
FIG. 2. Main figure shows EDXD spectrum for CsH at 25.1 GPa and $Ed = 41.301$ keV Å. Inset shows a portion of spectrum taken at $Ed = 78.396$ keV Å. Note appearance of higher $d$-spacing line (020). This was the highest $d$-spacing line detected. Bottom graph shows expected relative intensities for CrB structure as a comparison to the data at $Ed = 41.301$ keV Å.

taken at the high angle $Ed = 41.301$ keV Å. The bar chart below the main spectrum in Figure 2 illustrates the expected intensities for the CrB structure which is discussed below. The expected intensities were calculated by the procedure given in Ref. [14].

In the high angle experiment of Figure 2, at $Ed = 41.301$ keV Å, 21 peaks could be accounted for, with the general characteristics that $h + k = 2n$ for $hkl, k = 2n$ for $0kl, h, l = 2n$ for $h0l, h + k = 2n$ for $hk0, h = 2n$ for $h00, k = 2n$ for $0k0$, and $l = 2n$ for $00l$.

The coordination number of the $B1$ phase is 6. For $B2$, the coordination number for either the hydride or the alkali atom is 8. The orthorhombic structure was fitted with the CrB structure [15] with the Cs atom at the Cr position and the H atom at the B position [16]. The CrB structure has the $Cmcm$ space group, and both atoms have higher coordination than in the $B2$ structure [15,17]. This is consistent with the expected trend for equal or higher coordination in succeeding phases as pressure is increased. The $Cmcm$ space group is predicted to be a product space group of the CsCl parent structure in displacive phase transitions involving $X_5^+$ or $X_5^-$ mode softening [18]. The indexing to the CrB lattice was excellent and there were no unaccountable extra peaks. Further, the axial ratios observed are consistent with those of CrB at ambient conditions [15].

Table I shows values for the expected relative intensities for the CrB structure and the observed intensities for the typical spectrum of CsH in the orthorhombic phase with $Ed = 41.301$ keV Å from the fourth experiment. The expected intensities are computed by the procedure given in Ref. [14]. The discrepancy between the calculated relative intensities and the observed intensities can be attributed to texturing in the sample.

FIG. 1. Typical EDXD spectra for CsH in an experiment using ruby fluorescence to measure pressure.

TABLE I. Observed intensities for x-ray diffraction peaks of CsH at 25.1 GPa are compared to predicted intensities for the CrB structure at $Ed = 41.301$ keV Å.

| $hkl$ | $d_{obs}$ (Å) | $d_{calc}$ (Å) | $I_{obs}$ (Å) | $I_{calc}$ (Å) |
|---|---|---|---|---|
| 020[a] | 4.752 | 4.757 | 3.7[a] | 5.0[a] |
| 110 | 3.179 | 3.175 | 10.3 | 17.6 |
| 021 | 3.036 | 3.020 | 7.7 | 52.3 |
| 111 | 2.463 | 2.464 | 30.4 | 100.0 |
| 040 | 2.379 | 2.379 | 96.8 | 30.0 |
| 130 | 2.309 | 2.309 | 84.2 | 69.1 |
| 041 | 2.027 | 2.032 | 9.2 | 19.0 |
| 131 | 1.991 | 1.988 | 33.0 | 21.1 |
| 002 | 1.959 | 1.954 | 8.6 | 35.9 |
| 022 | — | 1.807 | — | 4.3 |
| 200 | 1.686 | 1.684 | 51.7 | 27.8 |
| 112 | }1.654 | 1.664 | }13.0 | 40.1 |
| 150 | | 1.656 | | 0.8 |
| 220 | }1.586 | 1.587 | }7.1 | 3.3 |
| 060 | | 1.586 | | 12.3 |
| 151 | 1.526 | 1.525 | 63.3 | 85.5 |
| 042 | 1.501 | 1.510 | 12.6 | 31.4 |
| 132 | 1.489 | 1.492 | 2.6 | 69.5 |
| 221 | }1.471 | 1.471 | }100.0 | 72.4 |
| 061 | | 1.469 | | 19.1 |
| 240 | 1.373 | 1.374 | 38.0 | 23.2 |
| 241 | — | 1.296 | — | 12.8 |
| 202 | 1.268 | 1.275 | 10.6 | 23.6 |
| 023 | 1.258 | 1.256 | 12.5 | 20.8 |

[a]The (020) peak was observed at $Ed = 78.396$ keV.Expected and observed intensities are calculated at this angle of diffraction.

The EDXD spectra for CsH at each pressure was fitted for relative unit cell volume. Consistent with earlier work [6,7] the $B1$ to $B2$ phase transition was observed to begin at 0.83 GPa in the first experiment and the observed change in relative volume was 8.4%. The orthorhombic phase first appeared at 18.9 GPa in the first experiment and at 16.3 and 17.3 GPa in the second and third experiments, respectively.

The data in the $B1$ and $B2$ phases from the first experiment is fitted to the first order Birch equation of state (EOS) [19] which is given by

$$P = \tfrac{3}{2} B_0 [(V/V_0)^{-7/3}$$
$$- (V/V_0)^{-5/3}][1 + \tfrac{3}{4}(B_0' - 4)((V/V_0)^{-2/3} - 1)].$$

$B_0$ and $B_0'$ are the zero pressure bulk modulus and bulk modulus derivative, respectively. $V_n/V_0$ represents the relative volume of the high pressure phase when extrapolated to zero pressure.

The data of the $B1$ phase was insufficient to permit a consistent two parameter fit, so the EOS fit was made with $B_0'$ held to 4.0 to compare with an earlier measurement of the EOS of this phase [6]. The parameters resulting from the EOS fit of the $B1$ and $B2$ phase data are (a) $B1$: $B_0 = 8.0 \pm 0.7$ GPa, $B_0' = 4.0$, and $V_n/V_0 = 1.0$;

and (b) $B2$: $B_0 = 14.2 \pm 1.0$ GPa, $B_0' = 4.0 \pm 0.2$, and $V_n/V_0 = 0.858 \pm 0.009$.

The previous measurements reported by Hochheimer et al. [6] were $7.6 \pm 0.8$ GPa, $4.0 \pm 0.4$ and $22.3 \pm 1.5$ GPa, and $4.8 \pm 0.5$ for $B_0$ and $B_0'$ of the $B1$ and $B2$ phases, respectively. Our current data is in agreement for the EOS fit to the $B1$ data. However, agreement for the $B2$ data is poor. Hochheimer et al. report $B_0 = 18.4 \pm 1.1$ GPa for the same phase in RbH. Systematically, $B_0$ increases monotonically for the $B1$ phase as we vary the alkali anion from Cs to Li [2,20]. We expect the same to occur in the $B2$ phase which justifies our measurements.

Figure 3 shows the data for relative volume versus pressure for CsH to the highest pressure measured. A first order Birch fit to the data yields for the orthorhombic CrB phase $B_0 = 21.6 \pm 0.1$ GPa, $B_0' = 4.7 \pm 0.1$, and $V_n/V_0 = 0.711 \pm 0.004$. At the average transition pressure of 17.5 GPa, the change in relative volume from the $B2$ phase to the orthorhombic phase is 6.3% using the $B2$ EOS parameters and the fit to the data of the orthorhombic phase of Fig. 3.

In the third experiment on CsH, using platinum for a pressure marker at the highest pressure of 253 GPa, the relative volume was measured as $V/V_0 = 0.260$. This is the highest pressure and compression ratio reached in the alkali hydrides to date.

The EOS for CsH was measured in three phases to 253 GPa. A new phase for CsH was observed beginning at 17.5 GPa and $V/V_0 = 0.53$. The new phase was assigned to the $Cmcm$ space group with the CrB lattice structure based upon the fit of 19 peaks from our energy dispersive x-ray diffraction data. The EOS of the new phase was measured to 253 GPa and $V/V_0 = 0.260$. This is a significantly high compression rivaled only by x-ray diffraction work on the rare gases, CsI, and the alkali metals. The bulk modulus of CsH at 253 GPa is 881 GPa
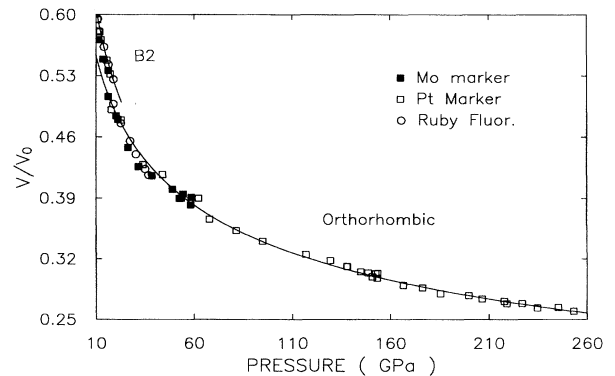
FIG. 3. Data from three separate experiments are plotted for $V/V_0$ vs pressure in the $B2$ and orthorhombic phases between 10 and 260 GPa. The upper solid line is the first order Birch-Murnaghan fit to the $B2$ data from the first experiment. The lower solid line is the fit to the data of the orthorhombic CrB phase for all three experiments.

compared to the value of 442 GPa for diamond [21] at atmospheric pressure.

The determination of the structure and the EOS provides theorists with the necessary information to make calculations on total energy, electronic structure, and phonon behavior which can be applied to our measurements of the EOS, the dispersion of the refractive index in the near infrared and the optical energy band gap to 251 GPa [22], and our measurements of the reststrahlen reflectivity of phonons to 251 GPa [23].

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