Phonon Softening and Elastic Instabilities in the Cubic-to-Orthorhombic Structural Transition of CsH

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The cubic-to-orthorhombic structural transition occurring in CsH at a pressure of about 17 GPa is studied by ab initio calculations. The relative stability of the competing structures and the transition pressure are correctly predicted. We show that this pressure-induced first-order transition is intimately related to a displacive second-order transition which would occur upon application of a shear strain to the (110) planes. The resulting instability is rationalized in terms of the pressure-induced modifications of the electronic structure.

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In recent years the availability of the diamond anvil-cell technology has renewed the interest in the high-pressure properties of alkali halides which are the simplest and prototypical among ionic solids. In the case of cesium halides, these studies have been carried out especially in the search of band-overlap metallization which occurs at pressures in the Mbar range. In the quest of metallization, unexpected phase transformations to tetragonal and orthorhombic structures have been observed experimentally and studied theoretically.

Metal hydrides are considerably more covalent than the corresponding halides. In fact, transition-metal hydrides are considered to be covalent materials, whereas alkali hydrides are structurally rather similar to the corresponding halides. Understanding the behavior of these materials at high pressure would presumably allow to better characterize the bonding properties of hydrogen in extreme pressure conditions and thus provide valuable hints towards the long searched goal of hydrogen metallization.

Alkali hydrides at zero pressure crystallize in the rocksalt (cubic B1) structure, while most of them undergo a transition to the cubic B2 (CsCl-like) structure at an applied pressure of a few GPa. Recently, a second transition from the B2 structure to a new orthorhombic phase has been observed to occur in CsH at an applied pressure of about 17 GPa. The new phase has been assigned the CrB structure which belongs to the space group.

In order to assess the driving mechanisms of the transition we have undertaken a series of first-principles calculations of the electronic, structural, elastic, and vibrational properties of CsH as well as of their dependence upon pressure. To this end, we have employed density-functional-theory (DFT) within the local-density approximation (LDA) and its gradient-corrected (GC) generalizations. Our calculations have been performed using norm-conserving pseudopotentials. In the case of Cs, 5s and 5p semi-core states have been treated as valence states. For LDA calculations we have used the same Cs potential as in Ref. while Hydrogen is described by a norm-conserving pseudopotential constructed for the 1s wave-function, so as to smoothen it somewhat and make our calculations well converged with the 25 Ry kinetic-energy cutoff which we use. New potentials have been generated for GC calculations. The vibrational properties are determined using the density-functional perturbation theory (DFPT) described in Ref.

In Table I we report our results for some structural properties of CsH in the three phases studied here: B1, B2, and CrB. The LDA fails to account for the stability of the rocksalt structure at zero pressure (negative B1 → B2 transition pressure), while GC calculations predict the correct sequence of transitions. GC-DFT also considerably improves the agreement between calculated and observed equilibrium lattice parameters and bulk moduli. The inclusion of Cs semi-core states in the valence manifold implies that the pseudopotential transferability is optimal around the corresponding orbital energies, rather than at the energies of the valence states. As a consequence, this treatment of semi-core states—although essential to obtain sensible results might require the use of more than one reference state in order.
to ensure optimum transferability. Whether or not the relatively poor quality of the LDA predictions is due to deficiencies in the Cs pseudopotential and the improvements achieved by using GC-DFT due to a fortuitous cancellation of errors is a matter which deserves further investigations. In any events, our results seem to confirm the importance of the gradient corrections to the LDA in the description of structural phase transitions, recently claimed in the case of the diamond to $\beta$-tin transition in silicon [18]. Both LDA and GC-DFT calculations correctly predict that a transition from the $B2$ to the CrB phases would occur at pressures somewhat larger than 10 GPa. In this case too, GC-DFT gives a value of the transition pressure in closer agreement with experiments (15 vs. 17 GPa). Note however that—due to hysteresis effects—the experimental estimate done when loading the sample [18] only provides an upper limit to the transition pressure. Also the volume discontinuity and the ratio between the transition volume and the equilibrium one are well reproduced by our calculations.

The CrB structure can be viewed as resulting from a continuous deformation of the cubic $B2$ structure in which a shear of the cubic edges in the (110) planes is coupled to a vibrational distortion of the atomic lattice, having the periodicity of a zone-border transverse phonon at the $M$ point of the Brillouin zone (BZ), $\mathbf{q} = (1/2, 1/2, 0)$, with symmetry $M_2^-$, and polarized along (001). In Fig. 1 we display how the distorted (110) plane (lower panel) results from the combination of the elastic (upper left) and the vibrational (upper right) deformations. In the ideal CrB structure the $a$ and $b$ crystallographic parameters indicated in Fig. 1 are in the ratio $b/a = 2\sqrt{2}$ which would be appropriate to a cubic structure. Due to the lower symmetry of the CrB structure with respect to the cubic one, the actual value of $b/a$ slightly differs from the ideal one and depends somewhat on pressure. This dependence is however very weak: at the transition pressure, for instance, one has $b/a \approx 2.9$. The third crystallographic axis is orthogonal to the $ab$ plane, and the corresponding crystallographic parameter has an ideal value $c = \sqrt{2}a$. The pressure dependence of $c/a$ is somewhat stronger than that of $b/a$: at the transition, for instance, one has $c/a \approx 1.3$.

In Fig. 2 we show the $T = 0$ enthalpy, $H = E + PV$, of the system constrained to a given elastic deformation, as a function of its amplitude which we measure through the parameter $t = \tan(\alpha) \times b/a$ [19]. We see that at any positive pressure a second minimum exists for $t = 1$, corresponding to the CrB orthorhombic structure. Actually, the exact value of $\alpha$ slightly depends on pressure because so does $b/a$. For pressures higher than $P^*_2 \approx 11$ GPa the second minimum becomes more stable giving rise to a first-order phase transition. The amplitude of the vibrational distortion, $u \equiv x/a$, which minimizes the enthalpy, $u_{\text{min}}$, depends on $t$, but for $t = 1$ it is constrained by symmetry to be $u_{\text{min}} = 1/4$, independent of pressure. The dependence of $u_{\text{min}}$ upon the amplitude of the elastic distortion, $t$, is shown in the inset of Fig. 2. We see
that \( u_{\text{min}} \) remains equal to zero up to a critical value of \( t = t^* \) which depends on pressure, and that it saturates to 1/4 for \( t = 1 \). This behavior is typical of the order parameter at a second-order phase transition, and it indicates therefore that a phonon frequency softens when the elastic distortion becomes larger than \( t^* \). In Fig. 3 we display the \( M_2^r \) phonon frequency as a function of \( t \) at different pressures, \( P \), and as a function of \( P \) for different elastic distortions.

The softening of the \( M_2^r \) frequency in correspondence to some value of the elastic distortion could have been expected on the basis of symmetry considerations. To see this, let us consider the crystal energy as a function of \( t \) and \( u \), \( E(t, u) \). Crystal symmetry requires that \( E(t, u) = E(t, \pm u) = E(t + 2, u + 1/2) = E(t + 2, u - 1/2) \). These relations imply that \( E(t, u) \) is stationary at the point \( (t, u) = (2, 0) \). This point lies in between the four equivalent minima at \((0, 0)\), \((2, \pm 1/2)\), and \((4, 0)\). Assuming that the energy landscape is simple, we arrive at the conclusion that \((2, 0)\) is a maximum. In particular, one has that \( \partial^2 E/\partial u^2 < 0 \), and hence there exists a value of \( 0 < t < 2 \) for which \( \omega_{M_2^r}^2 \sim \partial^2 E/\partial u^2 = 0 \). The orthorhombic phase corresponds to the \((1, 1/2)\) point in the \((t, u)\) plane which is also stationary because of symmetry. This point is located halfway between the two points \((1, 0)\) and \((1, 1/2)\) which are equivalent by symmetry and stationary with respect to variations of \( u \) \( (\partial E/\partial u = 0) \).

If \( t^* \) were larger than 1, \( \partial^2 E/\partial u^2 \) would be positive at \((1, 0)\) and \((1, 1/2)\), and therefore the assumption of a simple energy landscape would imply that \((1, 1/2)\) is a maximum with respect to \( u \), and the orthorhombic structure unstable. It is easy to see that a first-order transition with a discontinuous variation of \( u \) would occur in this case as the elastic distortion crosses \( t = 1 \). In fact, in this case the line \((t, 0)\) is stable with respect to variations of \( u \), up to \( t = 1 \). For \( t > 1 \) one has that \( E(t, 1/2) < E(t, 0) \). Hence, a discontinuous jump in \( u \) would occur at \( t = 1 \) where \( E(t, 1/2) = E(t, 0) \).

Arguments similar to those expounded above show that for \( t^* < 1 \) the \((1, 1/2)\) point is a minimum in the \( u \) direction, while nothing can be concluded in principle for other directions, but the fact that local stability is allowed. Our calculations indicate that in the present case \( t^* < 1 \) and that the CrB structure is indeed locally stable. For pressures higher than 11 GPa (15 GPa within GC), this structure is favored with respect to the cubic one, giving thus rise to a first-order transition.

The mechanisms driving the softening of the \( M_2^r \) phonon are related to the metallization of CsH under an applied pressure and/or shear deformation. At equilibrium \((P = 0, t = 0)\), the maximum of the valence band is practically degenerate between the \( R \equiv (1112) \) and \( X \equiv (001) \) points of the BZ, and the minimum of the conduction bands lies at the \( R \) point. A small applied pressure lifts the degeneracy between the valence-band maxima, rising the \( X \) point with respect to \( R \). The resulting fundamental band gap, \( E_g \), corresponds therefore to a \( X \rightarrow R \) transition, whose transferred momentum is \( M \equiv (1110) \), i.e. the wave-vector of the phonon which goes soft.

In Fig. 4 we display the electronic energy bands of CsH at \( P = 17.5 \) GPa, for \( t = 0 \) and for \( t = 0.3 \). In the distorted structure—corresponding to a non-vanishing value of \( t \)—the \( R \) and \( X \) points are folded to a same point of the BZ, and so are the \( \Gamma \) and \( M \) points. The gap, which is indirect in cubic symmetry, becomes thus direct in the distorted structure. We see that the elastic distortion considerably favors metallization, and thus enhances the screening of the phonon frequencies at the \( M \) point of the cubic BZ.

In Fig. 5 we display the dependence of \( E_g \) upon pressure and deformation angle. At small pressures, the \( M_2^r \) phonon frequencies softens almost for the same values of \( t \) for which the gap closes, whereas for pressure larger than \( \approx 18 \) GPa, it takes a larger value of \( t \) to soften the phonon frequency than to close the gap. If the bands were parabolic around the valence- and conduction-band edges, the phonon would go soft at the metallization. In fact, the independent-electron polarizability, \( \chi_0(q_M) \) would diverge logarithmically in this case [24], and the restoring force for a lattice distortion of wave-vector \( q_M \) would correspondingly vanish. If the valence and con-
FIG. 4. Electron energy bands of CsH close the fundamental energy gap (which is evidenced by the shadowed area) at an applied pressure of 17.5 GPa in the cubic structure (left) and under a finite shear deformation (right).

FIG. 5. Fundamental energy gap (eV) as a function of the applied hydrostatic pressure for different angles of deformation of the cubic structure (left), and as a function of the angle of deformation for different pressures (right).

duction bands have different shapes, the logarithmic divergence would no longer hold, and all that can be said in this case is that the more these shapes are similar, the more metallization contributes to the phonon softening. In any events, when the amplitude of the elastic distortion is larger than \( t^* \), the spontaneous vibrational distortion due to phonon softening re-opens the band gap and makes the orthorhombic phase insulating, in agreement with the behavior of \( E_g \) found in [2].

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The analysis which follows is based on calculations performed within the LDA. Our conclusions, of course, do not depend on the form of the exchange-correlation functionals.

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