

First Principles Study of Structural, Electronic and Elastic Properties of ScH and ScH₂

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Abstract— The Structural, electronic and elastic properties of ScH and ScH₂ are systematically studied by employing the density functional theory within generalized gradient approximation. The calculated lattice parameters are in agreement with the available results. Our calculated elastic constants explicitly indicate that these hydrides are mechanically stable. Elastic moduli, Poisson's ratio and Debye temperature are derived from elastic constants. The electronic structure reveals that the mono and dihydrides of scandium exhibit metallic behaviour at normal pressure. A pressure-induced structural phase transition from ZB to NaCl is observed at a pressure of 4.8 GPa for ScH.

Keywords: Ab-initio calculations; Structural phase transition; Electronic structure; Elastic properties.

1 INTRODUCTION

Metal hydrides have been attracting attention of scientists for decades. Their physical properties are interesting from both fundamental and practical points of view. Many transition metals react readily with hydrogen to form stable metal hydrides [1]. The photoemission and optical measurements by Weaver et al [2, 3] as well as improved electronic structure calculations of ScH₂ and YH₂ [4, 5] confirmed the band picture of the trivalent metal hydrides. First-principles study of the stability and electronic structure of metal hydrides were studied by Smithson et.al [6].

To the best of our knowledge, the structural properties of mono and dihydrides, the elastic constants of mono hydride of scandium are not yet reported. In our present work, we have investigated structural, electronic and elastic properties of different phases of ScH and ScH₂.

2 THEORETICAL FRAMEWORK

The total energy calculations are performed in the frame work of density functional theory using the generalized gradient approximation (GGA-PBE) as implemented in the VASP code [7]. Ground state geometries are determined by minimizing stresses and Hellman-Feynman forces using the conjugate-gradient algorithm with force convergence less than 10⁻³ eV Å⁻¹ and the Brillouin zone integration is performed with a Gaussian broadening of 0.1 eV. The cutoff energy for plane waves in our calculation is 600 eV. The valence electron configurations are Sc 4s² 3d¹, Y 5s² 4d¹, La 6s² 5d¹ and H 1s¹ atoms. Brillouin-zone integrations are performed on the Monkhorst-Pack K-point mesh with a grid size of 12x12x12 for structural optimization and total energy calculation. Iterative relaxation of atomic positions is stopped when the change in total energy between successive steps is less than 1 meV/cell.

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3 RESULTS AND DISCUSSION

3.1 Structural properties

The structural stability of ScH and ScH₂ is analyzed by calculating the total energy using VASP code based on density functional theory. The unit cell structures of the considered phases of ScH and ScH₂ are given in Fig. 1(a,b).

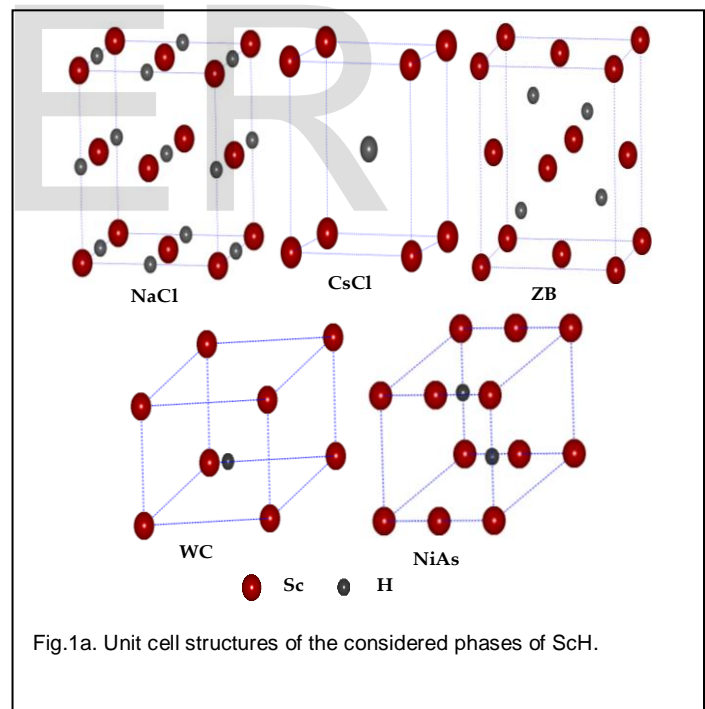


Fig.1a. Unit cell structures of the considered phases of ScH.

The lattice constants for the various structures of ScH and ScH₂ are optimized and their total energies (per unit cell) are calculated. The mechanical strength of a solid is determined with the help of its cohesive energy, which determines the strength of the binding between the constituent atoms in a solid. The cohesive energy of a solid is the difference between the total energy per atom of the bulk material at ambient condition and the atomic energies of the atoms belonging to the unit cell of the material:

$$E_{\text{coh}}^{\text{XH}} = [E_{\text{atom}}^{\text{X}} + E_{\text{atom}}^{\text{H}} - E_{\text{total}}^{\text{XH}}] \quad (1)$$

where E_{total}^{XH} is the total energy of the compound at the equilibrium lattice constant, E_{atom}^X and E_{atom}^H are the atomic energies of the pure constituent atoms.

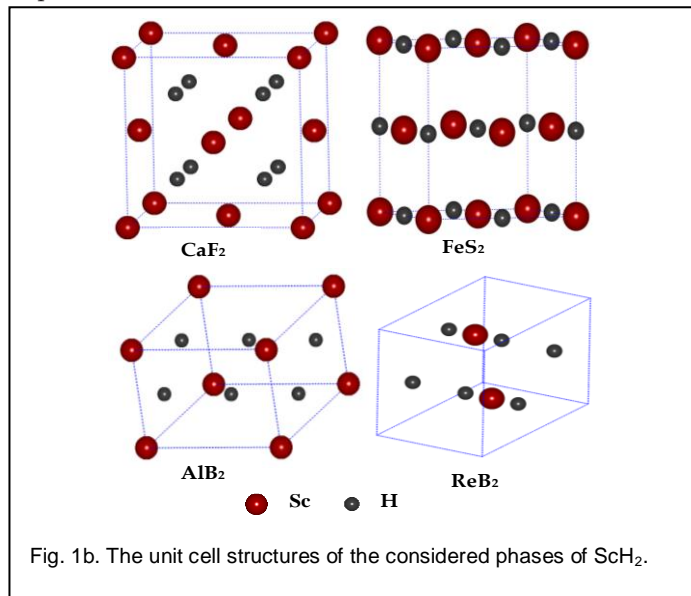


Fig. 1b. The unit cell structures of the considered phases of ScH₂.

The calculated ground state properties like lattice constant a_0 (Å), cell volume V_0 (Å³), cohesive energy E_{coh} (eV) and valence electron density ρ (electrons/Å³) for all considered phases of ScH and ScH₂ are given in Table (1) along with the other available experimental and the other theoretical data [6, 8-10]. The calculated lattice parameters are in agreement with the available results.

TABLE 1
 CALCULATED LATTICE PARAMETERS (Å), EQUILIBRIUM VOLUME V_0 (Å³), COHESIVE ENERGY E_{COH} (eV) AND VALENCE ELECTRON DENSITY (ELECTRONS/Å³) FOR ScH, ScH₂ FOR CONSIDERED STRUCTURES

Compounds	a	c	V_0	E_{coh}	ρ	
NaCl	4.5162	-	23.03	4.2383	0.1737	
CsCl	2.8805	-	23.9	3.1320	0.1674	
ScH	ZB	4.7245	26.36	4.3577	0.1518	
	NiAs	3.0633	4.9296	40.06	3.1327	0.0999
	WC	2.7937	4.4958	30.39	2.3538	0.1316
	CaF ₂	4.7561	-	26.90	7.7963	0.1859
ScH ₂	4.783 ^a					
	4.792 ^b					
	4.775 ^c					
	4.69 ^d					
	FeS ₂	3.7825	-	54.12	5.2495	0.0924
AlB ₂	2.7657	4.4999	29.81	3.4677	0.1677	
ReB ₂	3.1545	5.1639	44.5	4.9144	0.1124	

^aRef [8]
^bRef [9]
^cRef [10]
^dRef [6]

In order to determine the structural phase transition, enthalpy is calculated using the formula

$$H = E + PV \quad (2)$$

The transition pressures are calculated at which the enthalpies of the two phases are equal. Enthalpy versus pressure plots for different phases of ScH and ScH₂ are given in Fig. 2. It is observed that ScH is stable in the ZB phase at ambient pressure. On further increasing the pressure, ScH undergo a structural phase transition from ZB to NaCl phase at a pressure of 4.8 GPa. The metal dihydrides ScH₂ is highly stable in the CaF₂ phase at ambient and high pressure.

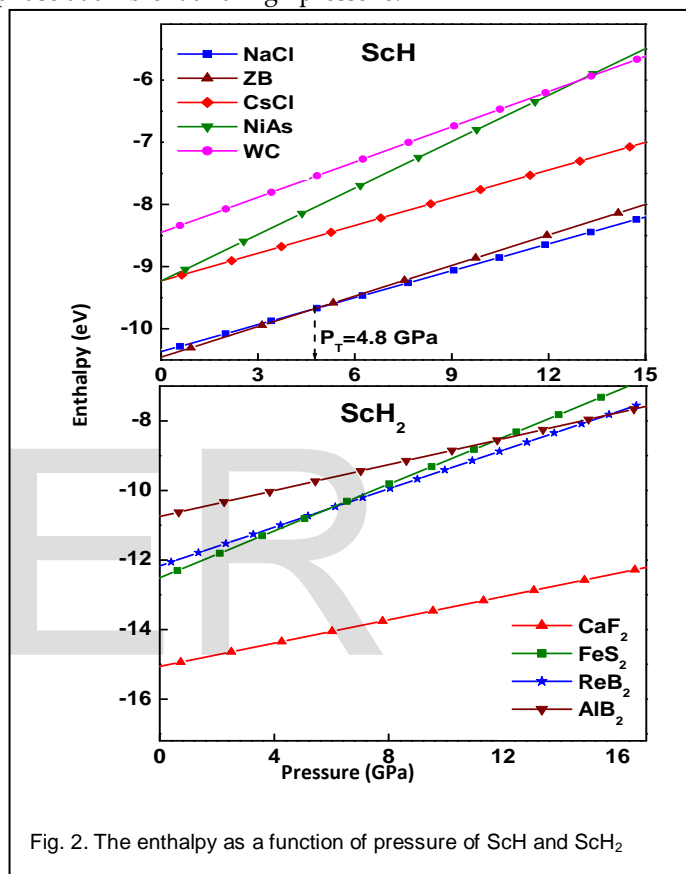


Fig. 2. The enthalpy as a function of pressure of ScH and ScH₂

3.2 ELECTRONIC PROPERTIES

In order to understand the electronic structure of ScH and ScH₂, total density of states (DOS) for stable structure is computed and is given in Fig. 3. The Fermi level is indicated by a dotted vertical line. The hydrogen s part of the DOS is mainly concentrated in the low energy region. In ScH, the hydrogen character is isolated within the lowest peak. This lowest peak possesses significant hydrogen character, in addition with a small Sc-d, Sc-s and Sc-p states. For the scandium hydrides, the Fermi level lies in the metal d states with the small contribution of Sc-p and Sc-s states and a very small contribution of H-s states. There is no energy gap between the conduction band and the valence band hence these hydrides are metallic. The d bands of the transition metal play the dominant role in electrical transport.

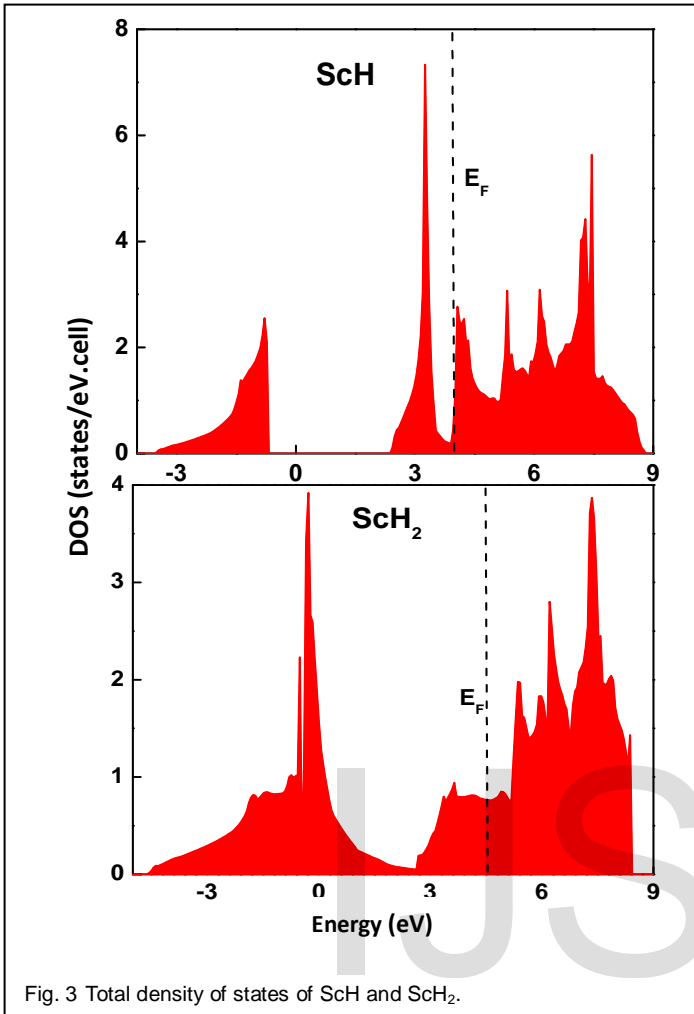


Fig. 3 Total density of states of ScH and ScH₂.

3.3 ELASTIC PROPERTIES

In order to calculate the elastic constants of a structure, a small strain is applied on to the structure and its stress is determined. The energy of a strained system [11, 12] can be expressed in terms of the elastic constants C_{ij} as:

$$\Delta E = \frac{E(\{e_i\}) - E_0}{V_0} = \left(1 - \frac{V}{V_0}\right) P(V_0) + \frac{1}{2} \left(\sum_{i=1}^6 \sum_{j=1}^6 C_{ij} e_i e_j \right) + O(\{e_i\}^3)$$

where V₀ is the volume of the unstrained lattice, E₀ is the total minimum energy at this unstrained volume of the crystal, P(V₀) is the pressure of the unstrained lattice, and V is the new volume of the lattice due to strain tensor [12].

The elasticity tensor has three independent components (C₁₁, C₁₂, C₄₄) for cubic crystals and five (C₁₁, C₁₂, C₄₄, C₁₃, C₃₃) for hexagonal crystals. A proper choice of the set of strains {e_i, i=1,2,...,6} in Eq.(3) leads to a parabolic relationship between ΔE/V₀ (ΔE ≡ E-E₀) and the chosen strain. While computing these energies all atoms are allowed to relax with the cell shape and volume fixed by the choice of strains {e_i}. The strain energy 1/2C_{ij}e_ie_j of a given crystal in Eq. (3) must always be positive for all possible values of the set {e_i}; for the crystal to be mechanically stable. The calculated elastic constants C_{ij} (GPa), Young's modulus E (GPa), shear modulus G (GPa) and

Poisson's ratio (ν) of scandium, NaCl and CaF₂ structure of ScH and ScH₂ are listed in Table (2). From tabulated values, it is found that most of the calculated elastic constants are in agreement with the available data [9, 13]. The small deviation in some elastic constants may be due to the small difference in the lattice constants calculated by different methods and also upon the various software packages used.

TABLE 2
 CALCULATED ELASTIC CONSTANTS C₁₁, C₁₂, C₄₄, C₁₃, C₃₃ (GPa), YOUNG'S MODULUS E (GPa), SHEAR MODULUS G (GPa) AND POISSON'S RATIO FOR ScH, ScH₂ FOR CONSIDERED STRUCTURES

	Sc	ScH	ScH ₂
	hcp	NaCl	CaF ₂
C ₁₁	74.75	126.05	159.55 105.17 ^b
C ₁₂	32.43	67.44	75.71 85.26 ^b
C ₄₄	18.79	70.05	77.59 93.20 ^b
C ₁₃	7.42	-	-
C ₃₃	94.68	-	-
B	37.64 43.5 ^a	86.97	103.66 91.90 ^b
E	73.31	133.71	157.83 59.90 ^b
G	31.19	53.75	63.32 28.83 ^b
B/G	1.21	1.62	1.64 1.53 ^b
ρ	0.175	0.244	0.2462 0.447 ^b

^aRef [13]

^bRef [9]

The Born-Huang elastic stability criteria [14] for the cubic crystals are

$$C_{44} > 0, C_{11} > |C_{12}|, C_{11} + 2C_{12} > 0 \quad (4)$$

and for the hexagonal crystals

$$C_{12} > 0, C_{33} > 0, C_{11} > C_{12}, C_{44} > 0 \quad (5)$$

$$(C_{11} + C_{12})C_{33} > 2C_{13}^2 \quad (6)$$

The computed values of the elastic constants for ScH and ScH₂ satisfy Born-Huang criteria suggesting that all are mechanically stable. The Young's modulus (E) and the Poisson's ratio (ν) values are two important factors necessary to find out the technological and engineering applications of a material. The Young's modulus (E) is given by

$$E = \frac{9BG}{(3B + G)} \quad (7)$$

Poisson's ratio is associated with the volume change during uniaxial deformation, which is expressed as

$$\nu = \frac{C_{12}}{C_{11} + C_{12}} \quad (8)$$

During elastic deformation no volume change occurs, if $\nu = 0.5$ and the material is incompressible. In addition, Poisson's ratio provides more information about the characteristics of the bonding forces than any of the other elastic constants. The ratio of bulk modulus to shear modulus is used to estimate the brittle or ductile behaviour of materials.

A high B/G value is associated with ductility, while a low B/G value corresponds to the brittle nature. The critical value which separates ductile and brittle materials is about 1.75. The calculated values of B/G predict that all considered structures of ScH and ScH₂ are brittle in nature.

The Debye temperature (θ_D) is the important parameter for determining the thermal characteristics of materials, which correlates many physical properties of materials, such as specific heat, elastic constants and melting temperature. The Debye temperature is defined in terms of the mean sound velocity v_m and gives explicit information about the lattice vibrations [15] and it is calculated using the equation [16]

$$\theta_D = \frac{\hbar}{k_B} \left[6\pi^2 n \frac{N_A \rho}{M} \right]^{1/3} v_m \quad (9)$$

with $\hbar = h/2\pi$, h is Planck's constant, k_B is Boltzmann's constant, N_A is the Avogadro's number, ρ is density, M is molecular weight, n is the number of atoms in the molecule and

$$v_m = \left[\frac{1}{3} \left(\frac{2}{v_t^3} + \frac{1}{v_l^3} \right) \right]^{-1/3} \quad (10)$$

Where

$$v_l = \left(\frac{B + 0.75G}{\rho} \right)^{1/2} \quad (11)$$

$$v_t = \left(\frac{G}{\rho} \right)^{1/2} \quad (12)$$

are the velocities of longitudinal and transverse sound waves respectively. The calculated Debye temperatures for the metal which are in agreement with the experimental results [13, 17] are listed in Table (3).

TABLE 3
 DENSITY (G/CM³), LONGITUDINAL VELOCITY (KM/S), TRANSVERSE VELOCITY (KM/S), AVERAGE VELOCITY (KM/S) AND DEBYE TEMPERATURE θ_D (K) FOR SCH, SCH₂

	Sc	ScH	ScH ₂
	hcp	NaCl	CaF ₂
ρ	2.018	3.241	2.837
v_l	6.266	6.866	8.063
v_t	3.931	3.903	4.622
v_m	4.249	4.339	5.134
θ_D	387.0	572.3	736.09
	360.0 ^a		
	346.0 ^b		

^aRef [13]

^bRef [17]

4 CONCLUSION

The structural, electronic and elastic properties of ScH and ScH₂ are investigated in detail. The computed equilibrium lattice parameters and bulk modulus values are consistent with the experimental and other available theoretical results. It is observed that ScH is stable in the ZB phase at ambient pressure. A structural phase transition from ZB to NaCl phase is predicted at a pressure of 4.8 GPa. The scandium dihydride is highly stable in the CaF₂ phase at ambient and high pressure. The electronic density of states of ScH and ScH₂ are metallic in nature.

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REFERENCES

- [1] Y. Fukai, Metal Hydrogen system: Basics Bulk Properties, Springer, Berlin, 2005
- [2] A. C. Switendick, Solid State Commun. 8, 1463, 1970
- [3] A. C. Switendick, Int. J. Quantum Chem. 5, 459, 1971
- [4] J. H. Weaver, R. Rosei, and D. T. Peterson, Phys. Rev. B 19, 4855, 1979; Solid State Commun. 25, 201, 1979
- [5] J. H. Weaver, D. T. Peterson, and R. L. Benbow, Phys. Rev. B 20, 5301, 1979
- [6] H. Smithson, C. A. Marianetti, D. Morgan, A. Van der Ven, A. Predith, and G. Ceder, Phys. Rev. B 66, 144107, 2002
- [7] G. Kresse, J. Furthmuller, Comput. Mater. Sci. 6, 15, 1996
- [8] W.M. Mueller, in: W.M. Mueller, J.P. Blackledge, G.G. Libowitz (Eds.), Hydrides of REM in Metal Hydrides, Academic Press, New York, 1968
- [9] T. Chihi, M. Fatmi, A. Bouhemadou, Solid State Sciences 14, 583 – 586, 2012
- [10] Suleyman Er, Dharendra Tiwari, Gilles A. de Wijs, and Geert Brocks, Phys. Rev. B 79, 024105, 2009
- [11] J. F. Nye, Physical Properties of Crystals, Oxford University Press, Oxford, 1985
- [12] S. Q. Wu, Z. F. Hou, Z.Z. Zhu, Solid State Commun. 143, 425, 2007
- [13] Charles Kittel, Introduction to solid state physics seventh edition 59 and 126, 2003
- [14] M. Born, K. Huang, Dynamical Theory of Crystal Lattices, Clarendon, Oxford, 1956
- [15] A.M. Ibrahim, Nucl. Instrum. Meth. B 34, 135, 1988
- [16] O. L. Anderson, J. Phys. Chem. Solids 24, 909, 1963
- [17] G.R. Stewart, Review of Scientific Instruments 54, 1-11, 1983