



Lattice Dynamical Properties of the Rare-Earth Dihydrides XH_2 ($X=Sc, Y,$ and La)

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Author's contribution

The sole author designed, analyzed and interpreted and prepared the manuscript.

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ABSTRACT

The rare-earth hydrides have received tremendous attention due to their potential applications for hydrogen storage technology, they exhibit intriguing electronic, optical, and mechanical properties. In particular, XH_2 series ($X= Sc, Y,$ and La), the prototype for rare-earth dihydrides, are very attractive due to their excellent properties: high pressure stability, mechanical strength, favourable kinetics feature, small neutron absorption cross-section, and dramatic optical properties. At ambient conditions, XH_2 ($X= Sc, Y,$ and La) crystallize in the cubic fluorite structure with a $Fm\bar{3}m$ space group, typically having a fcc lattice where the tetrahedral sites are filled with hydrogen atoms. The theoretical investigations of phonon properties of XH_2 are scarce as these properties are very helpful to explore the nature of XH_2 . Besides the structural aspects, the study of their vibrational properties is also important as they are closely related to several fundamental properties such as inter atomic interaction, phonon spectra, specific heat etc. Therefore, in this work a de launey angular force constant model has been used to study the phonons in XH_2 ($X= Sc, Y,$ and La) by considering the interatomic interactions up to third nearest neighbor. It is found that the ranges of phonon frequencies for acoustic and optical modes decrease gradually from ScH_2 to LaH_2 . The calculated results are compared and analyzed with available experimental results.

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1. INTRODUCTION

The hydrides of rare earth metals have been the object of many investigations due to their exceptional physical and structural properties that can be driven by the inclusion of hydrogen (hydrogenation). Therefore, a great interest has been keenly fostered in dealing with these compounds both experimentally and theoretically [1-10]. In particular, XH_2 series ($X=Sc, Y,$ and La), the prototype for rare-earth dihydrides, are very attractive due to their excellent properties: high pressure stability, mechanical strength, favourable kinetics feature, small neutron absorption cross-section, and also due to their potential applications for hydrogen storage technology. The rare earths (RE) absorb hydrogen readily and form systems which are amazing as concerns the richness of the observed physical phenomena. Similar to other group III rare earth metals, yttrium (Y), lanthanum (La), and scandium (Sc) at hydrogen pressures well below 1 atm forms a dihydride whose CaF_2 type crystal structure has all hydrogens occupying the tetrahedral interstitial sites of a face-centered cubic (fcc) metal sublattice [11]. Further the increase in hydrogen content results in filling the octahedral interstitial sites. As hydrogen atoms fill the octasites, electronic properties of the hydrides change gradually from metallic behavior characteristics of the dihydrides to a semiconducting one at hydrogen content higher than $REH_{2.7}$ [12]. The mono and dihydrides of the rare earth metals are metallic whereas its trihydrides are insulating or semi metals. The dihydride which is considered as an intermediate state toward trihydride during the hydrogenation process exhibits significant response against external parameters such as force and pressure along with the possible hydrogen transfer between the tetrahedral and octahedral interstitial sites for hydrogen accommodation [13].

The metallic behaviour of YH_2 and LaH_2 were reported by Huiberts et al. [1] experimentally by using by the thin-film technique. The electronic structure and optical properties of ScH_2 , YH_2 , and LuH_2 using optical absorptivity and thermos reflectance techniques in the photon energy range 0.2–5 eV between 4.2 and 340 K have been studied by Weaver et al. [7]. Recently, Machida et al. [2] studied the pressure induced disproportionation reaction of fcc LaD_2 at

pressures up to 18 GPa by using the synchrotron radiation X-ray diffraction (SR-XRD) method, similar pressure-induced reactions have been also observed for YH_2 , ScH_2 , and NdH_2 in XRD measurements. The mechanical properties of the bulk yttrium hydride fabricated by means of an ultrasonic pulse-echo method and the Vickers hardness indentation technique are studied by Setoyama et al. [8]. The band structures of ScH_2 and YH_2 have been investigated using the Korringa–Kohn–Rostoker (KKR) method based on the self-consistent or non-self-consistent fashion [9]. Wolf et al. [4] considered cubic phase and tetragonal phase, and obtained the crystal structure, the band structure and density of states (DOS) of metal dihydrides TH_2 ($T=Sc, Ti, V, Y, Zr,$ and Nb) using the self-consistent full potential-linearized augmented-plane-wave method (LAPW), but did not study the dynamical properties of TH_2 . Most of the studies have been concentrated on the energy band structures, optical properties, and other fundamental properties of XH_2 ($X= Sc, Y,$ and La) [1–6], however, too little is known about the vibrational properties of XH_2 , only the phonon dispersion relations of LaH_2 in 4 GPa have been computed [2]. This necessitated further theoretical studies in these systems. Detailed knowledge of the lattice dynamics is not only the prerequisite for any reliable calculations of the vibrational contribution to the surface free energy and influences the optical, thermo- dynamical properties etc., it also allows to check the dynamical stability of the system under study. Therefore, a systematic characteristic of the phonon dispersion relation of XH_2 ($X= Sc, Y,$ and La) is highly desirable. Hence, in this paper the zone centre phonons and phonon dispersion curves of XH_2 ($X= Sc, Y,$ and La) have been studied by applying de Launey angular force constant model [14] and are compared with other results.

2. STRUCTURE AND METHOD OF CALCULATION

Scandium is the lightest element of the group III transition metals. Similar to other group III metals—yttrium, lanthanum and most rare earths—scandium forms a fcc dihydride with a fluorite-type crystal structure at hydrogen pressures well below 1 atm [15]. The space group of XH_2 ($X= Sc, Y,$ and La) is $Fm\bar{3}m$ with atomic positions (0, 0, 0) for X and (0.25, 0.25,

0.25) and (0.75, 0.75, 0.75) and for H (shown in Fig. 1). The atomic density is 3 atoms per unit cell. The X atoms always form a fcc lattice with two H atoms occupy tetrahedral coordinate sites. There are nine (three acoustics and six optical) phonon branches as there are three atoms per unit cell in XH_2 . Group theoretical considerations classify the zone center frequencies in the following representations;

$$\Gamma : 2T_{1u} + T_{2g}$$

T_{1u} and T_{2g} are triply degenerate. Triply degenerate T_{2g} modes are Raman active modes and one of the T_{1u} modes corresponds to three acoustic branches. The remaining triply degenerate T_{1u} modes are infrared active mode. The T_{2g} modes describe the in-plane oscillations of H atoms while T_{1u} modes correspond to the combined out of phase movement of H atom in the XY plane. In order to elucidate the nature of the bonding and other thermal properties in these hydrides, the lattice dynamics of XH_2 (X= Sc, Y, and La) have been studied by using a de Launey type angular force constant (DAF) model [14].

In DAF model, the relative displacement of the reference atom and one of the neighbors is considered. The restoring force on the reference atom is taken to be proportional to the component of the relative displacement perpendicular to the line joining the two atoms at their equilibrium positions. The forces due to all neighbors are calculated separately and summed up together. Different force constants are used for the various categories of neighbors and the net force on the reference atom is obtained by summing over the contribution from all the

neighbors. In the present analysis three central force constants α_1 , α_2 and α_3 existing between X and H_1 or H_2 , H_1 and H_2 and $H_1 - H_1$ or $H_2 - H_2$, respectively, and the angular force constant α_1' between X and H_1 or H_2 and α_2' between H_1 and H_2 are taken into consideration for establishing a dynamical matrix of (9x9) for the fluorite structure. The central force constant between X-X is assumed to be the same as that between $H_1 - H_1$ or $H_2 - H_2$. The long wavelength limit method has been used to establish the analytical relation between the force constants and elastic constant. The expressions for the phonon frequencies at the zone centre and the analytical relation between elastic and force constants used in present investigation are given by the following equations;

$$4/3(\alpha_1 + 2\alpha_1') = [mM/(2m+M)]\omega_{TO}^2 \quad (1)$$

$$4/3(\alpha_1 + 2\alpha_1') + 4(\alpha_2 + 2\alpha_2') = m\omega_R^2 \quad (2)$$

$$2aC_{11} = 4/3(\alpha_1 + 2\alpha_1') + 4\alpha_2 + 12\alpha_3 \quad (3)$$

$$2aC_{12} = 4/3(\alpha_1 - 4\alpha_1') - 4\alpha_2' + 6\alpha_3 \quad (4)$$

$$2aC_{44} = 4/3(\alpha_1 + 2\alpha_1') + 4\alpha_2' + 6\alpha_3 - \{4/3(\alpha_1 - \alpha_1')\}^2 / \{4/3(\alpha_1 + 2\alpha_1')\} \quad (5)$$

Here M being the mass of X (X= Sc, Y, and La) atoms and m the mass of H, ω_{TO} represents the infrared optical frequencies whereas ω_R is the Raman active mode at the zone centre. By using the following results as given in Table 1 for zone centre (ZC) phonon frequencies [16] and elastic constants [17] to the above equations, the central and angular force constants are calculated and are listed in Table 2. The calculated ZC phonon frequencies are also listed in Table 2.

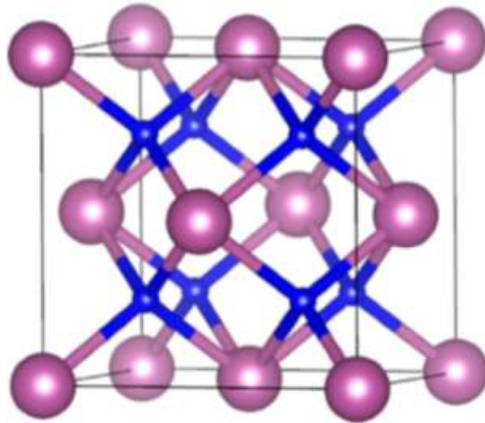


Fig. 1. XH_2 in the $Fm\bar{3}m$ CaF_2 structure type. Purple balls are X, blue hydrogen

Table 1. Input data

Compound	ZC phonon frequencies (cm ⁻¹) [16]		Elastic constant (10 ¹¹ dynes. cm ⁻²) [17]			Lattice constant (Å) [17]
	ω_{TO}	ω_R	C ₁₁	C ₁₂	C ₄₄	A
ScH ₂	976	1131	16.89	6.49	8.09	4.74
YH ₂	901	1049	13.38	5.94	6.96	5.20
LaH ₂	811	931	9.03	4.94	4.75	5.65

Table 2. Calculated force constants and zone centre (ZC) frequencies

Compound	Force constant (10 ⁴ dynes.cm ⁻¹)					ZC frequencies (cm ⁻¹)	
	α_1	α_1'	α_2	α_2'	α_3	ω_{TO}	ω_R
ScH ₂	3.223	0.436	0.408	0.0701	0.743	976	1131
YH ₂	3.003	0.279	0.059	0.2004	0.744	901	1049
LaH ₂	2.711	0.101	-0.197	0.2619	0.592	811	931

3. RESULTS AND DISCUSSION

It is clear from Table 2 that the interatomic interaction (α_1) between X (X= Sc, Y & La) and H₁ or H₂, is strongest for all hydrides as the bond length between these atoms are smallest compared to all other bonds. The interatomic interaction α_1 is largest for ScH₂ compared to other studied rare earth hydrides and it is due to its smallest value of lattice constant of ScH₂. It is also obvious from Table 2 that the calculated zone centre phonons of XH₂ (X= Sc, Y & La) are in excellent agreement with other calculated results [16]. It is also found from Table 2 that calculated phonon frequencies of infrared active modes T_{1u} and Raman active modes T_{2g} at the zone centre decrease gradually from ScH₂ to LaH₂. No experimental results are available for comparison. A thorough investigation of dynamic stability plays a vital role in determining various vibrational properties of materials. The phonon properties of XH₂ (X= Sc, Y & La) have been studied by applying short range force constant model [14]. The calculated phonon dispersion curves along three symmetric directions for XH₂ (X= Sc, Y & La) are shown in Figs. 2, 3 & 4 for ScH₂, YH₂ and LaH₂ respectively. The phonon spectra look roughly similar for three compounds. It is obvious from Figs. 2, 3 & 4 that there are three acoustic and six optic modes for all wave vectors along [KK0] directions. However, there are two acoustics and four optic modes along the high symmetry directions [K00] (Γ -X) and [KKK] (Γ -L) in all, due to the degeneracy of the transverse modes in both acoustic and optic branches. It is also visible from Figs. 2, 3 & 4 that all the optical modes of XH₂ (X= Sc, Y & La) are

found to be quite dispersive along the main symmetric directions. It is also obvious from this calculation that there is no splitting between longitudinal optical (LO) and transverse optical (TO) phonon branch at the zone centre, this supports their metallic properties without ionic displacement. The phonon dispersion relations as shown in Figs. 2, 3 & 4 possess three distinct regions.

The highest vibrational modes are due to H atoms whereas the vibrations of the X (X=Sc, Y, La) atoms play the most prominent role for lowest modes. There is a large difference between the frequencies of highest and lowest level vibration modes due to large mass ratio between X (X=Sc, Y, La) and H atoms and are in agreement with other theoretical calculation [18]. It is found from eigen vector displacement calculation that all optic phonon modes are due to H atoms while acoustic phonon modes are mainly characterized by the motion of X (X=Sc, Y, La) atoms. The present calculation does not give any imaginary phonon frequency modes along any symmetric directions for all these studied hydrides and this establishes that the structure is dynamically stable in cubic (Fm-3m) phase of XH₂ (X=Sc, Y, La). The comparison of phonon frequencies from Figs. 2, 3 & 4 reveals that the ranges of phonon frequencies for acoustic and optical modes decrease gradually from ScH₂ to LaH₂. The decrease of frequencies can be explained in terms of increasing total mass and increasing lattice parameter from ScH₂ to LaH₂ and is in agreement with other results [16].

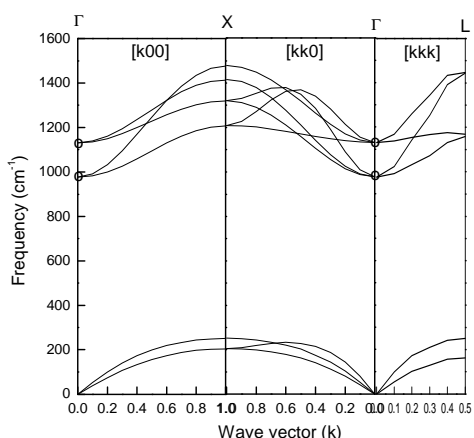


Fig. 2. Phonon dispersion curves of ScH₂. open circles are other theoretical results [16] at ZC

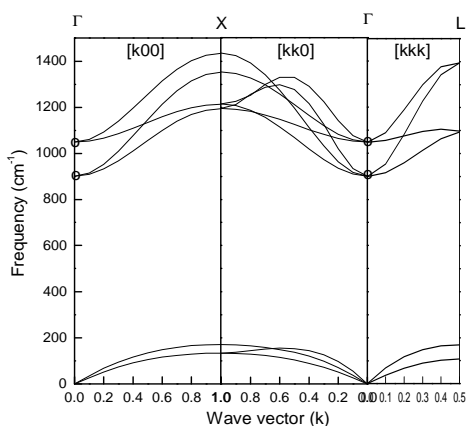


Fig. 3. Phonon dispersion curves of YH₂. open circles are other theoretical results [16] at ZC

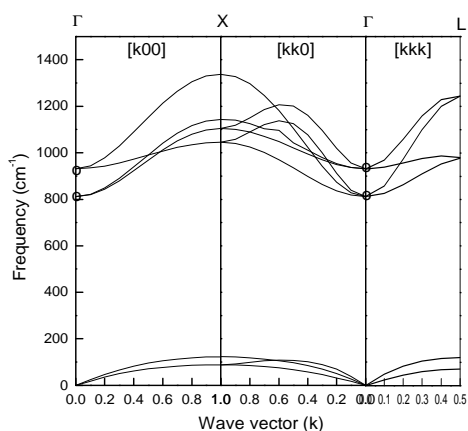


Fig. 4. Phonon dispersion curves of LaH₂. open circles are other theoretical results [16] at ZC

4. CONCLUSIONS

This work presents a systematic study of the vibrational properties of XH₂ (X=Sc, Y, La) compound in its fluoride phase. The phonon calculation gives a phonon band gap which divides the phonon band structure into two major regions. The low-frequency modes below this gap are mostly associated with the heavy X (X=Sc, Y, La) atoms. The H atom vibrations above the phonon band gap dominate the high frequency region. It is also demonstrated that XH₂ (X=Sc, Y, La) with cubic fluorite structure is dynamical stable. The calculated results are in good agreement with available other theoretical results.

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COMPETING INTERESTS

Author has declared that no competing interests exist.

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