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Thermodynamic functions from lattice dynamic of $KMgH_3$ for hydrogen storage applications

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ABSTRACT

The dynamic and the thermodynamic properties of $KMgH_3$ have been investigated by density functional theory (DFT). We have found that the calculated lattice parameters differ from the experimental data by less than 0.6% and the electronic density of states (DOS) reveals that the $KMgH_3$ is an insulator. The formation energy of $KMgH_3$ from binary hydrides (MgH_2 and KH) has been calculated. Using density-functional perturbation theory, we have calculated the phonon dispersion curves, the phonon density of states, the Born effective charge tensors, the dielectric permittivity tensors and the phonon frequencies at the center of the Brillouin zone of $KMgH_3$. Also we have assigned the calculated phonon frequencies at the gamma point for Infrared-active and Raman-active modes. For the first time, the thermodynamic functions are computed using the phonon density of states.

1. Introduction

In the past decade the need for clean, renewable, and efficient energy sources has became important with time. Hydrogen is the most promising energy carrier for the future [1,2]. However, an efficient way of storing hydrogen, especially for mobile applications, remains a challenge. Conventional ways to store hydrogen such as gas compression and liquefaction are massive, expensive and necessitates important security issues, and therefore numerous diverse ways to store hydrogen have been proposed [3].

Light weight hydrides are possible candidates for future hydrogen storage materials, it is why they have received considerable attention in the recent literature [4]. The technical challenge is to find materials that exhibit the best combination of thermodynamics and kinetics for hydrogen desorption and absorption, and to have the ability to store a sufficient percentage of hydrogen by weight and volume [2,5].

Mg-based compounds receive special attention because of their light weight and low cost. Other perovskite compounds of the $MMgH_3$ (M is a metal) have been investigated theoretically by several authors [6,7]. Vajeeston et al. [6] have found that $MMgH_3$ compounds are wide-band-gap insulators and the chemical bonding of these compounds is highly ionic. Only $KMgH_3$ is reported with the ideal Pm3m structure [8].

Ghebouli et al. [9] have studied the structural, elastic, electronic, optical and thermal properties (heat capacity and Debye Temperature) of $KMgH_3$ by employing pseudo-potential plane-wave approach based on the density functional theory (DFT). In the same time, Reshak and co-workers [10] have investigated the structural and the elastic properties of $KMgH_3$ to search the stability of perovskite-type in three different phases using FP-LAPW method within a framework of DFT. Also, they have studied [10] the electronic and optical properties for only stable perovskite-type $KMgH_3$. These works shows that $KMgH_3$ have an indirect gap X-R. However, Ghebouli et al. [9] considered the $KMgH_3$ as an insulator with a gap of 2.52 eV, while Reshak and co-workers [10] considered $KMgH_3$ as a semiconductor with a gap of 2.53 eV.

Bouamrane et al. [11] have determined calorimetrically the standard enthalpy of formation of $KMgH_3$. Recently, Komiya et al. [12] have reported the synthesis and decomposition of $KMgH_3$. They have found that the $KMgH_3$ is decomposed in a single-step reaction as follow:

$$KMgH_3 \rightarrow K + Mg + (3/2)H2.$$

Besides that, no experimental or theoretical data about thermodynamics functions and lattice dynamics of $KMgH_3$ are available. In order to contribute in this field, the full phonon-dispersion curves will be necessary for a microscopic understanding of the lattice

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dynamics. Indeed, the phonon spectrum knowledge has a significant role in determining various material properties such as the phase transition, thermodynamic stability, transport and thermal properties [13].

In this paper we will study the structural, lattice dynamical and thermodynamic properties of $KMgH_3$ using the first-principles method within local density approximation. The phonon frequencies at the Brillouin zone center, the phonon dispersion curves and the thermodynamic properties are calculated.

2. Computational details

The calculations were performed according to the density functional theory [14] using the plane wave implementation of the ABINIT code [15]. We have used the norm conserving pseudopotentials [16], where the K (3p, 4s), Mg (3s) and H (1s) orbitals are treated as valence states. The electronic wave functions were expanded in plane waves up to a kinetic energy cutoff of 80 Hartree. Integrals over the Brillouin zone were approximated by sums of 6 × 6 × 6 mesh of special k-point [17]. The exchange-correlation is evaluated within the local density approximation [18] by using Ceperly–Alder homogeneous electron gas data [19].

The phonon modes, dielectric tensors, and Born effective charge tensors are evaluated using the linear-response method in the frame of density functional perturbation theory [20–22]. Further details can be found in our previous work [13].

3. Results and discussion

3.1. Crystal structure

The ideal cubic perovskite structure of $KMgH_3$ compounds (space group 221) contains one formula with the following Wyckoff positions of the atoms: K 1a (0, 0, 0), Mg 1b (0.5, 0.5, 0.5) and H 3c (0, 0.5, 0.5) [8]. The only degree of freedom that must be relaxed is therefore the lattice constant a. After minimization, we have obtained a value of 4.046 Å for the lattice constant. This value is in good agreement with the experimental value of 4.023 Å. The discrepancy is less than 0.6%. This is largely sufficient to allow the further study of electronic, dynamical and thermodynamic properties.

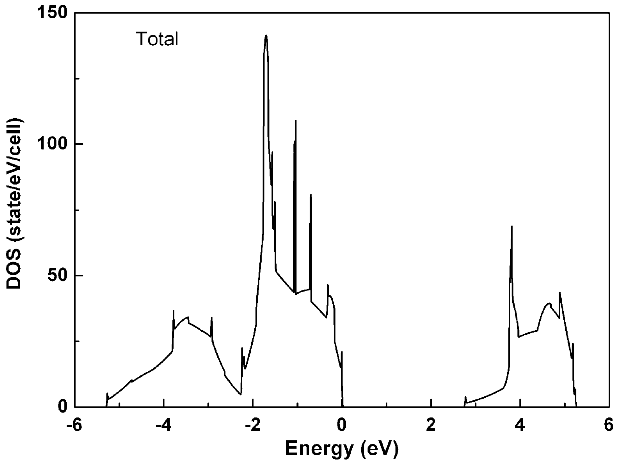

Fig. 1. The electronic density of state of $KMgH_3$. The Fermi level is set to zero energy.

3.2. Electronic properties

The total density of states (DOS) at the optimized parameters for the ground-state structure of the $KMgH_3$ compounds is displayed in Fig. 1. The site projected density of states (PDOS) is illustrated by Fig. 2.

The $KMgH_3$ compound has a finite energy gap ($E_g = 2.8\,\text{eV}$) between the valence band (VB) and the conduction band (CB).

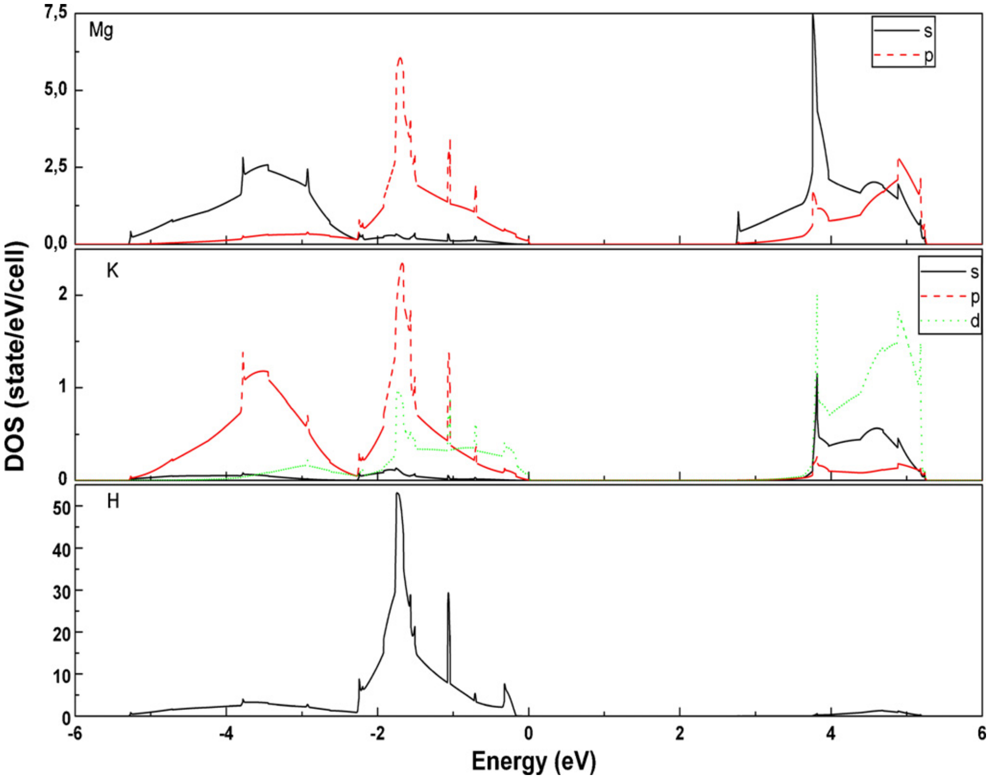

Fig. 2. Projected density of state for $KMgH_3$. The Fermi level is at zero energy.

Table 1
Calculated hydride formation energy (ΔH) according to Eqs. (1)–(4).

Enthalpy of reactions	This work	Cal.	Exp.
$\Delta H1$(kJ/mol)	−28.40	−32.23 [6]	
$\Delta H2$(kJ/mol)	−88,92	−74.87 [6]	
$\Delta H3$(kJ/mol)	−106.95	−96.02 [6]	
$\Delta H4$(kJ/mol)	−167.47	−138.67 [6]	−165 ± 6 [12]

Therefore, $KMgH_3$ can be considered as an insulator. As it can be seen on Fig. 2, the PDOS of K has a very small contribution to the VB. Also, there is a clear hybridization between H-s and Mg-s states in the region from −5.5 eV to −0.25 eV. This hybridization indicates that the covalent bond nature remains between Mg and H ions. Therefore, the interaction between K and MgH_6 units is pure ionic whereas the interaction between Mg and H contains an ion-covalent component.

3.3. Enthalpy of formation

In general, synthesis of $KMgH_3$ compounds from an equiatomic KMg matrix is not possible since the alkali metals (here is K) and magnesium are immiscible in the solid and liquid state.

The possible reaction pathways are:

$$KH + MgH_2 \rightarrow KMgH_3 \quad (1)$$

$$K + MgH_2 + 1/2\,H_2 \rightarrow KMgH_3 \quad (2)$$

$$KH + Mg + H_2 \rightarrow KMgH_3 \quad (3)$$

$$K + Mg + 3/2\,H_2 \rightarrow KMgH_3 \quad (4)$$

The enthalpy of the formation is calculated by taking the difference between total electronic energy of the products and the reactants. The ground state energies of K, KH and MgH_2 have been computed for ground state structure, viz. in space group Im3m for K, Fm3m for KH and $P4_2/mnm$ for MgH_2, all with full geometry optimization.

The results are listed in Table 1. We notice that the calculated enthalpies are in good agreement with the theoretical published values [6]. Also, our calculated enthalpy, using reaction (4), is in good agreement with the experimental value [12].

3.4. Lattice dynamic and Born effective charge

Table 2 presents the calculated Born effective charges and the optical dielectric constant. The K and Mg atoms are located at centers of cubic symmetry so that their effective charge tensors are isotropic. The H atoms are located at the face centers and thus have anisotropic effective charge.

In the cubic structure, the optical dielectric tensor is reduced to scalar. However, it must be noted that local density approximation usually overestimates the optical dielectric constant [23].

The calculated frequencies of Γ-point phonons are reported in Table 3. Since there are 5 atoms in the primitive unit cell of $KMgH_3$ crystal, it will be 15 normal vibration modes at the Γ point: 3 acoustic and 12 optical phonon modes.

Table 2
The Born effective charge tensors and optical dielectric constant of $KMgH_3$.

	xx	*yy*	*zz*
Z_K	0.941	0.941	0.941
Z_{Mg}	1.892	1.892	1.892
Z_{H1}	−1.23	−0.801	−0.801
Z_{H1}	−0.801	−1.23	−0.801
Z_{H1}	−0.801	−0.801	−1.23
ε	3.75	3.75	3.75

Table 3
The calculated Γ-point phonon frequency (cm^{-1}) of $KMgH_3$.

Mode	Frequency (cm^{-1})
T_{1u}	204.7
T_{1u}: *TO*	636.04
LO	690.83
T_{2u}	884.30
T_{1u}: *TO*	1159.64
LO	1249.34

Based in the factor group theory, the irreducible representations at Γ point is: $4T_{1u}+T_{2u}$ each of them triply degenerated where T_{1u} and T_{2u} are IR-active and silent respectively. For IR-active modes there are LO–TO splitting due to the coupling of the atomic displacement with the long-range electric field by means of Born effective charges tensors [13].

The phonon dispersion curves for $KMgH_3$ along several high-symmetry lines are plotted in Fig. 3. We note first that there are three separate bands which are due to the large mass difference between H atoms and (K, Mg) atoms. Second, the $KMgH_3$ is dynamically stable since throughout the Brillouin zone all phonon frequencies are positive.

3.5. Thermal properties

The thermodynamic functions of $KMgH_3$ can be determined by the entire phonon spectrum. In the present work, the phonon contribution to the Helmholtz free energy F, the phonon contribution to the internal energy E, the entropy S and the constant-volume specific heat C_v, are calculated using the following formulas within the harmonic approximation [24] at a given temperature T:

$$F = k_B T \int_0^{\omega_{\max}} \ln\left(2\sin h\left(\frac{\hbar\omega}{2k_B T}\right)\right) g(\omega)d\omega \quad (5)$$

$$E = \frac{\hbar}{2}\int_0^{\omega_{\max}} \omega \coth\left(\frac{\hbar\omega}{2k_B T}\right) g(\omega)d\omega \quad (6)$$

$$S = k_B \int_0^{\omega_{\max}} \left[\frac{\hbar\omega}{2k_B T}\cot h\left(\frac{\hbar\omega}{2k_B T}\right) - \ln\left(2\sin h\frac{\hbar\omega}{2k_B T}\right)\right] g(\omega)d\omega \quad (7)$$

$$C_v = k_B \int_0^{\omega_{\max}} \left(\frac{\hbar\omega}{2k_B T}\right)^2 csch^2\left(\frac{\hbar\omega}{2k_B T}\right) g(\omega)d\omega \quad (8)$$

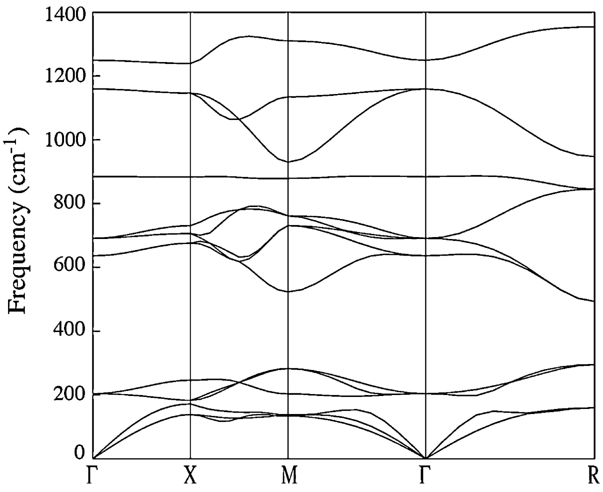

Fig. 3. Calculated phonon dispersion curves along symmetry lines for $KMgH_3$.

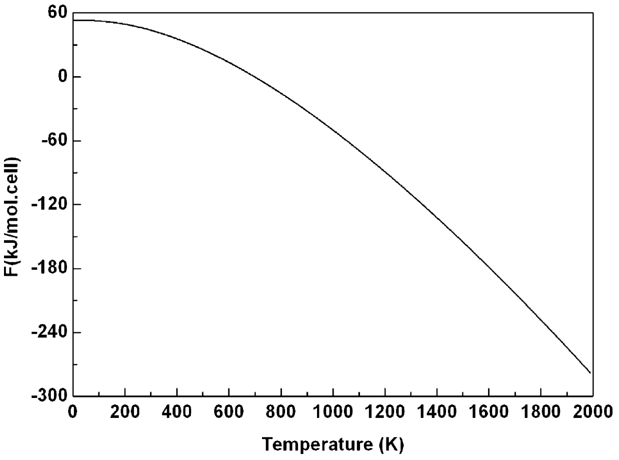

Fig. 4. The calculated phonon contribution to the Helmholtz free energy *F*.

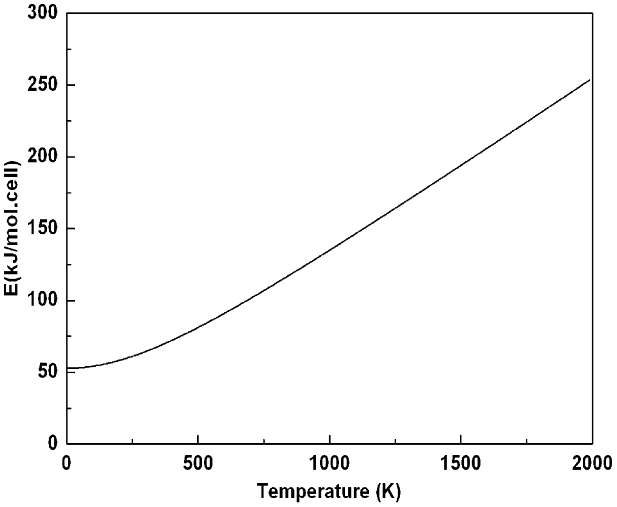

Fig. 5. The calculated phonon contribution to the internal energy *E*.

where k_B is the Boltzman constant. $\omega_{\max}$ is the largest phonon frequency. $g(\omega)$ is the normalized phonon density of states with $\int_0^{\omega_{\max}} g(\omega)d\omega = 1$.

The functions F, E, S and C_v are shown on: Figs. 4–7 respectively. We notice that when the temperature increases, the calculated F of $KMgH_3$ decrease gradually where the calculated E, S increase continually. The value of F and E at zero temperature, that represent the zero-point motion [25], is 55 kJ/mol.

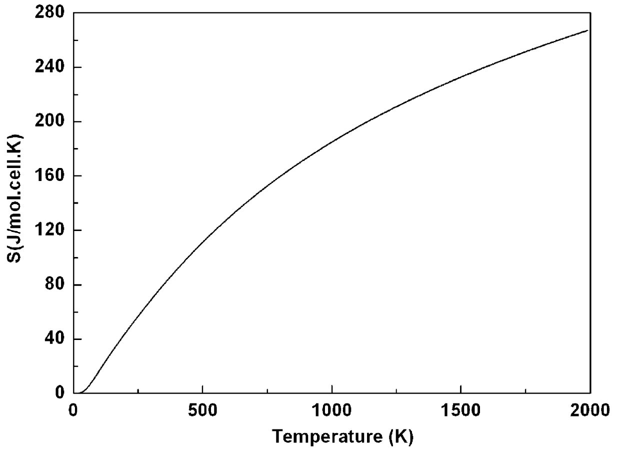

Fig. 6. The calculated phonon contribution to the entropy *S*.

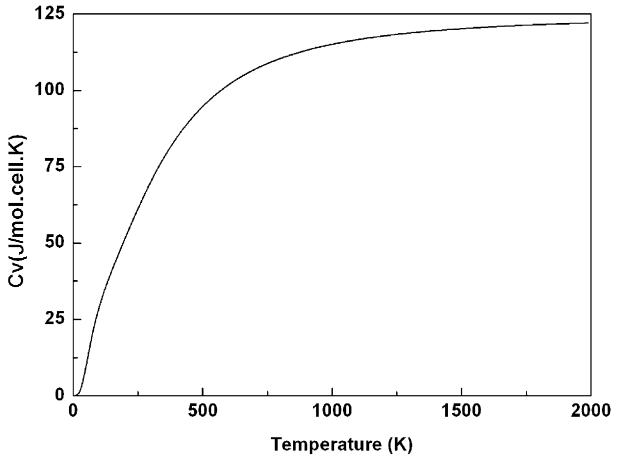

Fig. 7. The calculated phonon contribution to the constant-volume specific heat C_v.

The calculated C_v exhibits the expected T^3 power-law behaviour in the low-temperature limit. At high temperature C_v reaches a classic limit of 125 J/mol cell K which is in good agreement with the classic law of Dulong–Petit [25]. In fact, two known limiting cases are correctly predicted by the elastic continuum theory [26]: (i) at low temperatures, C_v is proportional to T^3 [25] (ii) at high temperatures the constant volume heat capacity C_v tends to the Petit and Dulong limit [25].

Unfortunately, no experimental values of C_v of $KMgH_3$ are found. Our calculated values can be seen as a prediction for future investigations.

4. Conclusion

The dynamical and thermodynamic properties of $KMgH_3$ are presented and calculated using density functional theory. We have first optimized the lattice parameters. The calculated lattice parameters differ from the experimental data by less than 0.6%. The calculated density of state shows that the $KMgH_3$ is an insulator. The Formation energy of the $KMgH_3$ is calculated for different possible reaction pathways. The determined phonon frequencies at the zone (gamma point) for the infrared modes are assigned. Finally, using the calculated phonon density of states, the thermodynamic functions are determined with the harmonic approximation. To the best of the author's knowledge, no experimental values of the thermodynamic functions of $KMgH_3$ are found. Our calculated values can be seen as a prediction for future investigations.

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