Journal of Alloys and Compounds 509S (2011) S857–S859

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Ab initio lattice dynamics of CoH and NiH

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ARTICLE INFO

Article history:
Received 26 July 2010
Received in revised form
23 September 2010
Accepted 26 September 2010
Available online 6 October 2010

Keywords:
Hydrides
Ab initio
Lattice dynamics
Thermodynamics

ABSTRACT

Ground state parameters and lattice dynamics of CoH and NiH phases are studied by means of the state-of-the-art ab initio pseudopotentials methods. Calculated ground state parameters and phonon DOS are in rather good agreement with available experimental data. No phase transformation for CoH and NiH was found in a wide pressure and temperature range.

1. Introduction

Metal hydrides are of great interest materials from both technological and scientific point of view. Indeed, their experimental and theoretical studies can shed light to understanding of chemical bonding in simple hydrides, thus, promote designing of hydrogen storage materials. Besides, they are also interesting from geophysical point of view, as they exhibit a phase transition if subjected to high pressure [1,2]. Ni-H system shows the isomorphic phase transition $\gamma_1 \rightarrow \gamma_2$ (fcc) under hydrogen pressure [2,3]. The γ_1 phase can be both paramagnetic and ferromagnetic, whereas the γ_2 phase is paramagnetic down to 4.2 K [4]. In contrast to Ni-H, Co-H system has polymorphic phase transitions and its T–P diagram shows the presence of ε (hcp)-, γ_1- and γ_2-phases. At pressures above 7 GPa, a hydride with $x \sim 1$ is formed on the base of the high-temperature fcc (γ) cobalt modification [5,6]. Cobalt and its hydrides are ferromagnetic [7].

In the present work, we have performed ab initio studies of the ground state parameters and lattice dynamics of CoH and NiH in B1, NiAs, DHCP type phases where hydrogen atom occupies an octahedral interstitial position and ZnS where hydrogen atom occupies a tetrahedral interstitial position. These crystalline phases are subjected to high pressure and high temperature via the quasi-harmonic approximation to understand the possibility of a phase transition in NiH and CoH.

2. Calculation procedure

We have performed pseudopotential plane-wave based ab initio calculations in the framework of density functional theory [8,9] and density functional perturbation theory [10] through the Quantum ESPRESSO code [11]. The generalized gradient approximation in the Perdew–Burke–Ernzerhof parametrization [12] was chosen to treat the exchange-correlation effects because it is known to reproduce correctly ground state parameters for a wide range of crystals. Nonlinear core correction has been included in pseudopotentials used as it is obligatory when one deals with high pressure phases. The integration over the Brillouin zone was performed by using the special k-points technique [13] with a broadening of 0.025 Ry according to the Marzari–Vanderbilt cold-smearing scheme [14]. We used $14 \times 14 \times 6$, $14 \times 14 \times 14$, $14 \times 14 \times 8$ and $14 \times 14 \times 14$ k-meshes, for DHCP, NaCl, NiAs and ZnS structures of hydrides, respectively. Force constants were obtained by means of eight dynamical matrices for all the structures considered. We applied plane waves (PW) with the cutoff energy up to 50 Ry to mimic electronic wave functions in a periodic crystal, and cutoff energy up to 500 Ry to describe the augmented charge. All calculations were performed with spin-polarized electrons. The ratio between the hexagonal a-axis and c-axis (c/a) for the HCP and DHCP structures were optimized and all the atomic positions were relaxed for each volume. Free energies for the hydrides are obtained using the equation $F(V,T) = E_{tot}(V) + F_{vib}(V,T)$, where $E_{tot}(V)$ is the static energy of a crystal at a given volume, and $F_{vib}(V,T)$ is the phonon contribution defined as $F_{vib}(V,T) = k_BT\int d\omega g(\omega) \ln\left[2 \sin h\left(\hbar\omega/2k_BT\right)\right]$, $g(\omega)$ is the phonon density of states. Thermodynamic properties of the hydride phases are calculated using the QHA code [15].

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doi:10.1016/j.jallcom.2010.09.164

Table 1
Calculated ground state parameters and magnetic property of B1 NiH and CoH.

Parameter	CoH	NiH
Lattice parameter (Å)	3.735 (our calc.) 3.7124 (exp.) [18]	3.717 (our calc.) 3.72 (exp.) [16,17] 3.65 (calc) [19]
Bulk modulus (GPa)	200 (our calc.) –	196 (our calc.) 198 (calc) [20]
Magnetic moment (μ_B)	1.29 (our calc.) 1.3 [21]	0 (our calc.) 0 (exp) [24]

3. Results and discussion

First we present results of ab initio calculations for ground state parameters which are shown in Table 1 where they are compared with available data. For B1 NiH our calculated lattice parameter, $a_0 = 3.717$ Å, is in excellent agreement with experimental one [16,17]. The difference between calculated equilibrium and experimental volume for B1 NiH is only of about 0.24%, while for B1 CoH [18] the difference is about 1.84%. Note, despite such a kind rather small difference for CoH, we used the experimental lattice parameter to calculate interatomic force constants, thus, phonon dispersion relations and related thermodynamic properties. Smaller lattice parameter, 3.65 Å, obtained by Elsasser et al. [19], can be explained as a result of the use of LDA type exchange-correlation potentials in their calculations. Experimental data on the ground state parameters of hydrides are very scarce. At the same time, for B1 NiH our calculated B_0 is in good agreement with B_0 by Wimmer [20]. In accordance with experimental results our spin-polarized calculations showed that B1 NiH is nonmagnetic, while B1 CoH is magnetic. Calculated magnetic moment at experimental lattice parameter matches perfectly experimentally obtained moment [21] (see Table 1). Theoretical magnetic moment of B1 CoH decreases almost linearly depending on applied pressure with the slope of about $-0.1\ \mu_B/\text{Å}^3$.

As one can see phonon dispersion relations in both B1 CoH (Fig. 1a) and NiH (Fig. 2a) do not show any peculiarity for transversal acoustic modes. The main difference between these modes is almost degenerate TA_1 and TA_2 modes for B1 CoH in the ΓX [1 1 0] direction. A noticeable difference is also softening of longitudinal LA mode for B1 CoH in ΓX [1 0 0] direction and its flattening near the W-point. It is worth noting that the modes resemble these for B1 FeH obtained in Ref. [1], as the mass difference for metals is quite small. The largest difference is less than 5% between Fe and Ni, and atomic mass for Co and Ni is almost the same. Despite close atomic mass, optical modes for B1 CoH and NiH are quite different, as they are more dispersive for NiH, that the fact that Co and H are bonded stronger in comparison to NiH.

We compared experimental phonon density of states for acoustic modes in NiH with calculated one and observed rather good agreement between them (see Fig. 2b). As concerns optical modes, the maximum of dynamical structure factor is located around 102 meV [18] and 89 meV [22] for CoH and NiH. The experimental value for CoH is somewhat higher than our calculated maximum for phonon DOS for the optical modes. Besides, for NiH we obtained two well defined peaks, in contrast to experimental result of Kolesnikov et al. [23]. The discrepancy can be ascribed to imperfectness of experimental samples and temperature factor, while our DFT calculations are done at $T = 0$ K. At elevated temperatures anharmonic effects play an important role, as it was shown for in Refs. [25,26].

Some useful thermodynamic properties are provided in Table 2. One can see that the amplitude of hydrogen vibration in the hydrides is quite large and an order of magnitude is larger than that for metals (Co or Ni). The comparison of the volume expansion coefficient and Debye temperature also judge that atomic bonding in CoH is stronger that the one in NiH.

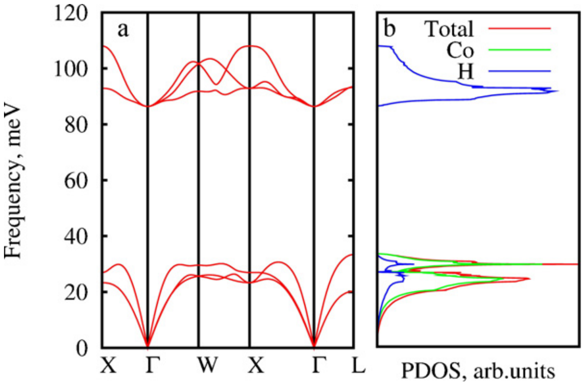

Fig. 1. Phonon dispersion relations (a) and phonon density of states (b) in B1 CoH at experimental lattice parameter.

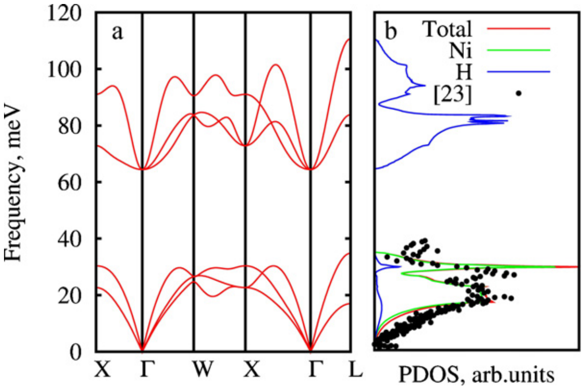

Fig. 2. Phonon dispersion relations (a) and phonon density of states (b) in B1 NiH at theoretical lattice parameter. Filled circles refer to experimental date and taken from [23].

Table 2
Selected thermodynamic properties of B1 CoH and NiH.

Hydride	T (K)	C_v^{vib} (R)	α_v (Å^3 K^{-1})	Θ_D (K)	$\langle U^2 \rangle$ (Å^2)	
					Me	H
CoH	5	0.0001	–	735.16	0.003601	0.126091
	150	2.4292	2.5605E−05	721.35	0.005419	0.170547
	300	3.9869	4.4774E−05	928.83	0.009327	0.255105
	500	5.0331	5.8246E−05	995.70	0.014979	0.383305
NiH	5	0.0003	–	551.90	0.004805	0.107872
	150	2.5601	3.2899E−05	679.83	0.008242	0.163461
	300	4.1572	5.8230E−05	842.67	0.014696	0.248619
	500	5.1362	7.6098E−05	892.00	0.023828	0.376184

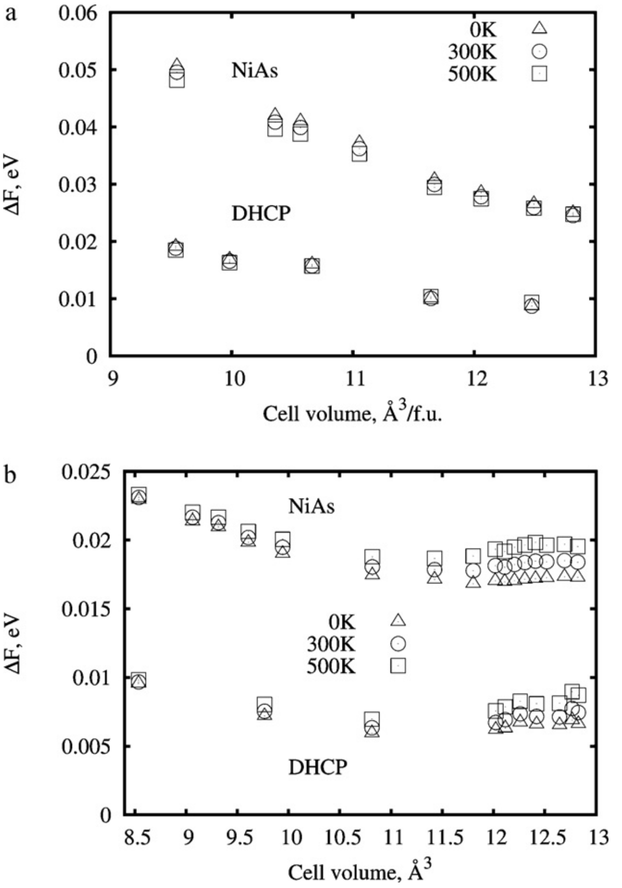

Fig. 3. Free energy difference F(NiAs/DHCP)—F(B1) for CoH (a) and NiH (b) respectively (the volume range correspond to 0–130 GPa for CoH and 0–200 GPa for NiH). The abscissa stands for the B1 phase.

We also were interested in whether a phase transition, like in FeH [1], takes place for CoH and NiH at high pressure ranges. In order to shed light to this, we have calculated free energies of different phases for the hydrides as a function of the cell volume and temperature (Fig. 3). The difference between free energies is shown with respect to B1-phase of CoH (Fig. 3a) and NiH (Fig. 3b). One can see that B1 phase has the lowest energy difference irrespective of temperature (up to 500 K) and we conclude that there is no phase transition in the pressure ranges considered, up to 130 GPa for CoH, and 200 GPa for NiH. The conclusion is in agreement with result of experiment [27] where no structure change was observed at pressures up to 123 GPa. For ZnS structure the difference is larger, so, we did not show it in the figures.

4. Conclusions

To conclude, we have studied ground state parameters, lattice dynamics and free energies for different crystalline phases of CoH and NiH by means of first-principles methods using ab initio pseudopotentials. We found good agreement between calculated parameters and available theoretical and experimental data. Theoretical phonon DOS for NiH captures all specific behaviors of experimentally measured phonon DOS for the acoustical branches. According to free energy difference no phase transition is found for both the hydrides in the wide pressure and temperature range.

Acknowledgments

The authors thank RFBR (#10-02-01410) for financial support. E.I.I thanks also Swedish Foundation for Strategic Research (SSF), and Goran Gustafsson Foundation. M.P.B. was partially supported by the Programme of Creation and Development of the National University of Science and Technology “MISiS”.

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