The Bonding of Interstitial Hydrogen in the NiTi Intermetallic Compound

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The interstitial hydrogen bonding in NiTi solid and its effect on the metal-to-metal bond is investigated by means of the EH tight-binding method. Electronic structures of octahedral clusters Ti_4Ni_2 with and without hydrogen in their centers are also calculated using the cluster model. The metal d states that interact with H 1s are mainly metal-metal bonding. The metal-metal bond strength is diminished as the new metal-hydrogen bond is formed. The causes of this bond weakening are analyzed in detail.

Key Words : Metal hydrides, Electronic structure, Bonding

Introduction

The intermetallic compound NiTi, which is the prototype of alloys exhibiting a shape memory behavior, is intensively studied over the world.[1] Apart from the shape memory phenomenon, this type of alloy is of scientific and technological interest in view of the great potential for practical applications such as hydrogen storage media for fuel cells, electrodes for rechargeable batteries, and energy conversion materials.[2-4] This compound may be utilized as one of promising hydrogen storage materials for the development of a future clean energy system because it absorbs hydrogen readily under convenient conditions of pressure and temperature and forms a hydride.

Structural studies of hydrides of NiTi have been initiated by Noreus *et al*.[5] More recently, the structure of the hydrides $NiTiH_x$ (x = 1.0 and 1.4) has been resolved, including hydrogen positions, from powder neutron diffraction data.[6] The results of these structural investigations established the existence of a tetragonal metal atom structure corresponding to the space group I4/mmm and led us to undertake a theoretical investigation of the electronic structure of NiTiH which was compared with that of the pure intermetallic compound NiTi.

There are several papers related to the electronic structure of NiTi.[7-11] However, the study of hydrogen interaction with NiTi alloy is rather scarce. The lack of such investigations is probably due to the very poor understanding of the positions of hydrogen atoms in the hydrides. The investigation of the band structure for hydrogenated NiTi is important to reveal the origin of chemical bonding in NiTi alloy and its interaction with H as an impurity in the extended structure. In the present work we have examined the changes in the electronic structure of the pure intermetallic due to the metal-hydrogen interactions when H is incorporated into the NiTi lattice. All the calculations are of extended Hückel (EH) type,[12] using the tight-binding method.[13] The parameters are listed in Table 1.

Table 1. Extended Hückel Parameters[15]

atom	orbital	H_{ii} (eV)	$\zeta_1{}^a$	$C_1{}^a$	ζ_2	C_2
Ti	4s	−6.3	1.50			
	4p	−3.2	1.50			
	3d	−5.9	4.55	0.4206	1.40	0.7839
Ni	4s	−7.8	2.10			
	4p	−3.7	2.10			
	3d	−9.9	5.75	0.5683	2.00	0.6292
H	1s	−13.6	1.30			

[a] Exponents and coefficients in a double-ζ expansion of the 3d orbital.

We report the electronic and bonding structures of NiTi alloy with the CsCl-type structure. The effect of incorporating H as an impurity on the Ni-Ni, Ti-Ti, and Ni-Ti bonding is also analyzed with aid of density of states (DOS) and crystal orbital overlap population (COOP). Within the formalism of simple perturbation theory the interaction of two levels, ΔE, is given by eq. (1).[14] The magnitude of the matrix element H_{ij} in the numerator is related to the overlap of the relevant orbitals,

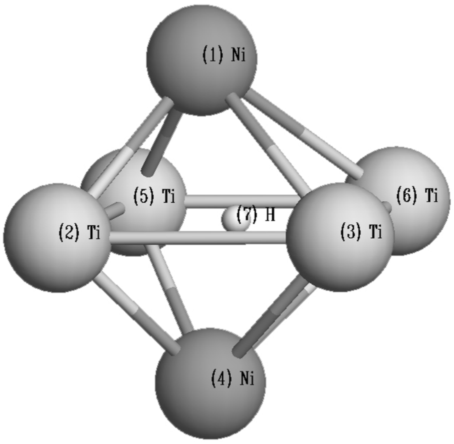
$$\Delta E = |H_{ij}|^2/(E_{jo} - E_{io}) \qquad (1)$$

and the denominator tells us that the interaction is greater the closer in energy the two orbitals are. The consequence of orbital interactions between the metal band and the hydrogen orbital can be traced down and analyzed by examining DOS curves. Contributions or projections of specific orbitals are particularly helpful. A COOP curve allows us to determine if a collection of energy levels contributes to bonding or antibonding between two atoms. In other words the COOP is indicative of the nature and the strength of a particular interatomic interaction within the unit cell. We find that both the DOS and COOP curves, in particular their combination, are very effective in analyzing the bonding properties of solid lattice. The use of these tools will be demonstrated throughout the paper. The electronic charge distribution is analyzed by means of Mulliken population analysis. The main purpose of this work is to obtain more insight into a qualitative bonding picture of interstitial hydrogen within NiTi, considering that the EH method can provide more detailed information regarding electronic properties of the system under investigation.

Crystal Structure

The high temperature phase of unhydrided NiTi alloy has a cubic CsCl structure with the unit-cell dimension a = 2.998 Å. The structural investigations of hydrides of NiTi indicate that only a few of the 16 Ti atoms in the tetragonal unit cell are very slightly shifted from their ideal positions in the cubic CsCl structure of pure NiTi, while the Ni atoms are much more displaced. This would correspond to a slightly expanded NiTi lattice (parameters a = 6.216 Å and c = 12.326 Å) due to the absorption of hydrogen in the cubic unit cell, which is about 10.5% expansion in the volume. The hydrides do not present any structural phase transition as a function of temperature, in contrast to the parent alloy NiTi. The crystal space group is I4/mmm.

The H atoms are located at two different octahedral sites H1 and H2 which are coordinated with two Ni and four Ti atoms. The hydrogen atoms in H1 sites occupy preferably the 16n sites in the crystal lattice with the space group I4/mmm. This site corresponds to the central site of the octahedron, the corners of which are occupied by four Ti atoms and two Ni atoms. The octahedra that coordinate H1 are formed by four titanium atoms with Ti-H distances in the range of 2.11-2.25 Å and two nickel atoms with Ni-H distances of 1.78 Å (see Scheme 1). As shown in Scheme 1, this hydrogenated cluster model is constructed on the basis of the crystal structure of NiTiH. The interatomic distances between atoms in the cluster are listed in Table 2. We perform molecular orbital calculations on this cluster to examine how hydrogen 1s level is affected by its surrounding metal atoms. As a first approach to the calculations of the electronic band structure of NiTi hydrides we have assumed a full occupancy of the H1 sites leading to a maximum content of an H atom per formula unit, that is, making the stoichiometry NiTiH, since two H2 positions are at too short a distance to be occupied simultaneously. This simplifying assumption leads us to consider a unit cell which contains 16 formula units of NiTiH. The tetragonal structure of NiTiH used in the calculations is represented in Figure 1.



Scheme 1

Table 2. List of interatomic distances in HM_6 (Å)

Atom	Ni (1)	Ti (2)	Ti (3)	Ni (4)	Ti (5)	Ti (6)	H (7)
Ni (1)		2.594	2.810	3.494	2.722	3.016	1.781
Ti (2)			3.081	2.594	3.115	4.376	2.254
Ti (3)				2.810	4.231	3.108	2.107
Ni (4)					2.722	3.016	1.781
Ti (5)						2.871	2.124
Ti (6)							2.125

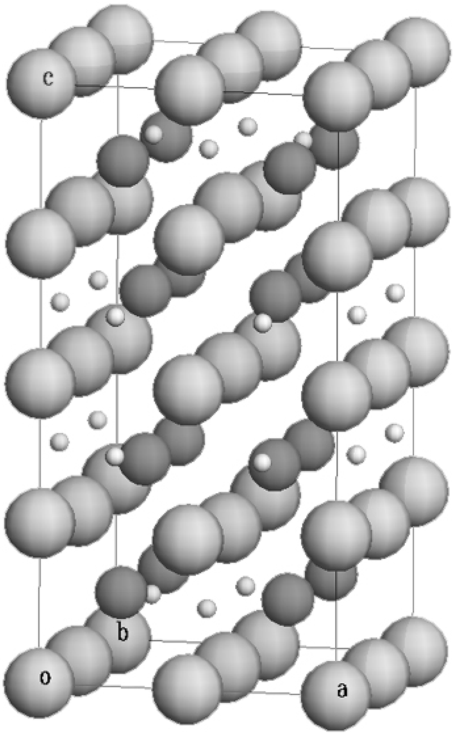


Figure 1. Structure of NiTiH. The large circles represent Ti, the dark medium circles Ni, and the small circles H atoms.

Results and Discussion

Electronic structure of NiTi. Let us first discuss the electronic structure of pure NiTi alloy. Figure 2 shows the total and projected DOS curves calculated for the cubic CsCl phase of NiTi. In the DOS of the bulk 3D solid the major contribution of the Ni d states is found at low energies, the main peak corresponds to rather localized states situated between –11 and –9 eV, while the main contribution of the Ti d states, which are more delocalized, result in a broad structure located at higher energies between –7 and –3 eV. A substantial number of s and p states penetrate the d bands. The d band dispersion of Ni is much smaller than that of Ti, reflecting the more contracted nature of the Ni d orbital. As is typical for electron poor compounds, the Fermi level resides at low-energy part of the conduction band composed in this case mostly of Ti d orbitals, with some contribution from Ni orbitals. The existence of a Ti contribution to the narrow 3d Ni band shows covalent mixing of the Ti orbitals with the Ni orbitals. If we look at the detailed composition of

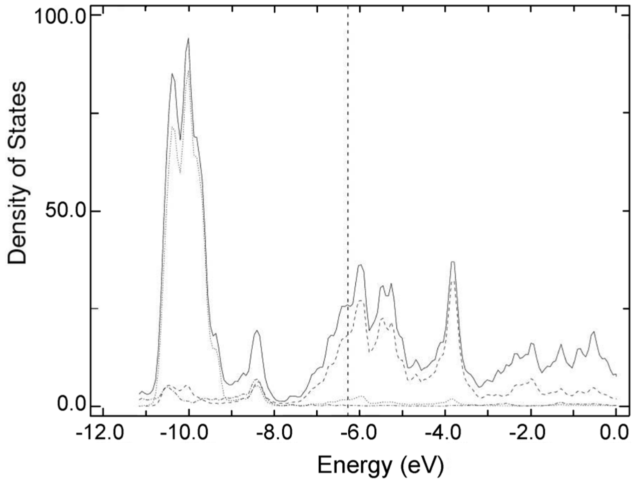


Figure 2. Total and projected densities of states for the CsCl-type structure of NiTi. Vertical line represents the Fermi level. Solid line is total DOS; dotted line is Ni d contribution, dashed line Ti d contribution, and dash-dot line shows the Ni s contribution.

the Ni atoms in the unit cell, we obtain the orbital population $d^{9.51}$ $s^{1.06}$ $p^{0.38}$. Note that on average any Ni atom has its s band approximately 1/2 filled. In the case of Ti the value for the orbital population is $d^{2.17}$ $s^{0.65}$ $p^{0.23}$. The Ni atoms are negatively charged with respect to the Ti. It is useful to remember that when two metals with different Fermi energies are placed in contact, electrons will flow from the metal with higher Fermi energy to the metal with a lower Fermi level. This means that the electron transfer from more electropositive Ti atoms takes place toward the Ni atoms.

Regarding the bonding, COOP analysis gives additional insights related to the bond and its strength. The COOP curves of the Ti-Ti, Ni-Ti, and Ni-Ni interactions are shown in Figure 3. In both Ni and Ti metals the bottom of the d band is metal-metal bonding and the top metal-metal antibonding. For the majority of the COOP for the Ni-Ti bonding the Fermi level is situated slightly below empty antibonding levels; consequently these corresponding bonds are very strong and therefore responsible for the stability of the structure. The Ti-Ti interactions are bonding until –5.3 eV. The Ti-Ti bonds also contribute significantly to the region at the Fermi level. However, the net overlap population (OP) for Ni-Ni bonds falls slightly into negative region, making these bonds least stable in the structure. The calculated Ni-Ti OP value (0.226) is much higher than that of Ti-Ti (0.163) and Ni-Ni (-0.010) bonds. The Ni-Ti interaction seems to be strongly bonding.

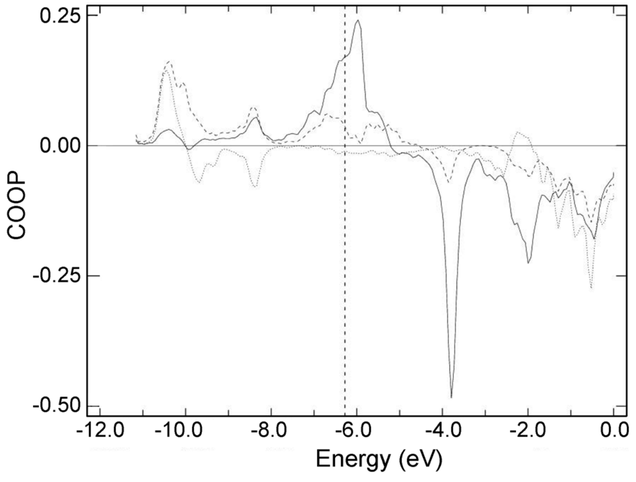


Figure 3. COOP curves for the CsCl-type structure of NiTi. Interactions in the upper part are bonding (+), in the lower part antibonding (−). Solid line is Ti-Ti interaction, dotted line Ni-Ni interaction, and dashed line Ni-Ti interaction.

The effect of interstitial H on the electronic structure of NiTi. The hydrogen absorption in NiTi alloys is a favorable process. As explained earlier, the crystal lattice of NiTi expands by the hydrogenation. It is stressed here that in this system, any substantial changes of the crystal structure do not occur during the hydrogenation except for the onset of lattice expansion and distortion. In other words, the hydride structure is the derivative one of the parent compound, and hydrogen atoms occupy a part of the octahedral interstitial sites in the crystal lattice of the compound. For the NiTiH tetragonal structure the binding energy of 5.27 eV per formula unit, $E_{NiTi} + E_H - E_{NiTiH}$, is obtained at the octahedral H1 interstitial site. It is therefore of great interest to investigate how the chemical bonding between atoms in NiTi is modified by hydrogen incorporation. So, further calculations are carried out in the following two cases by using the crystal structure shown in Figure 1.

The first case is the calculation for pure NiTi structure without any hydrogen atoms. In Table 3, this case is denoted as NiTi (expansion). The second case is the calculation for NiTi hydride with hydrogen atoms. Needless to say, lattice expansion induced by hydrogenation is counted explicitly in these calculations. This is done to see only the electronic effect of interstitial hydrogen on the bond strength changes in the NiTi hydride. The DOS and COOP curves for the first case are shown in Figures 4 and 5, respectively. They show the similarities to those for the CsCl-type structure of NiTi. We have found no a significant difference in their electronic structures. The Ni orbital composition is $d^{9.53}$ $s^{1.06}$ $p^{0.35}$ whereas for Ti the composition is $d^{2.16}$ $s^{0.66}$ $p^{0.24}$. The resulting Fermi energy is calculated to be –6.41 eV. Both metal-metal overlap populations, Ni-Ti and Ti-Ti, are 0.204 and 0.171, respectively. The Ni-Ni interaction appears to be nonbonding (OP = 0.026).

As a good starting point for the analysis of the second case, we need to perform the molecular orbital calculations on HM_6 (M_6=Ti_4Ni_2) octahedral cluster to examine how both the Ti-Ni and Ti-Ti interactions which are strong enough to hold the metal framework are affected by the metal-hydrogen bonding. Shown in Figure 6 is the schematic interaction diagram for HM_6 cluster (Scheme 1) built from the crystal structure of NiTiH. At infinite separation both the metal framework and the hydrogen are neutral. The hydrogen 1s orbital at −13.6 eV is singly occupied. For the composite system HM_6, the lowest energy level at –14.8 eV is the hydrogen bonding level resulting from a strong interaction between 1s (H) and the orbitals near the bottom of the d

Table 3. Electron density, overlap population (OP), charge, and distances for NiTiH tetragonal structure

Structure	Atom or bond	Electron density[a]			Charge	OP[a]	Distance (Å)	E_F (eV)
		s	p	d				
NiTi								−6.28
	Ni	1.06	0.38	9.51	−0.95	−0.010	2.998	
	Ti	0.65	0.23	2.17	0.95	0.163	2.998	
	Ni-Ti					0.226	2.596	
NiTi(exp)								−6.41
	Ni	1.06	0.35	9.53	−0.92	0.026	2.72-2.76	
	Ti	0.66	0.24	2.16	0.18-1.19	0.171	2.87-3.29	
	Ni-Ti					0.204	2.48-3.02	
NiTiH								−6.37
	H	1.53			−0.53			
	Ni	0.89	0.38	9.52	−0.77	0.004	2.72-2.76	
	Ti	0.47	0.21	2.02	0.65-1.68	0.126	2.87-3.29	
	Ni-Ti					0.160	2.48-3.02	
	H-Ti					0.103	2.11-2.25	
	H-Ni					0.102	1.781	

[a] Average value.

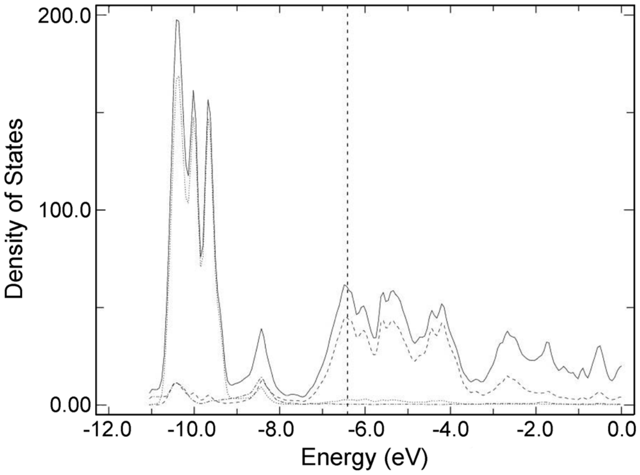


Figure 4. DOS curves for NiTi sublattice after H absorption. Vertical line represents the Fermi level. Solid line is total DOS; dotted line is Ni d contribution, dashed line Ti d contribution, and dash-dot line shows the Ni s contribution.

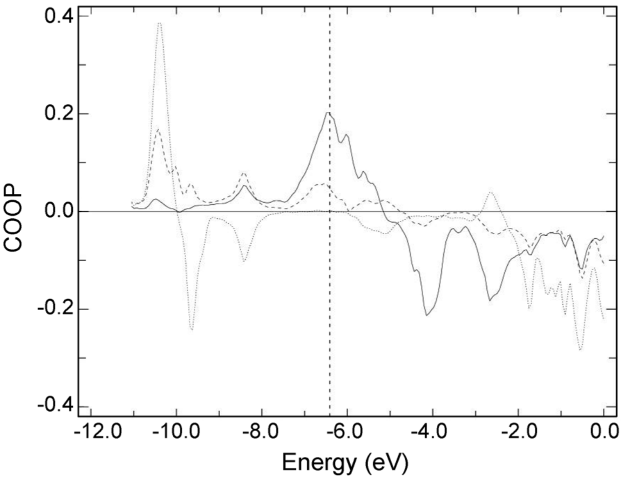


Figure 5. COOP curves for NiTi sublattice after H absorption. Interactions in the upper part are bonding (+), in the lower part antibonding (−). Solid line is Ti-Ti interaction, dotted line Ni-Ni interaction, and dashed line Ni-Ti interaction.

band corresponding basically to the “a_{1g}” orbital expected for an approximately octahedral metal ligand framework (M_6). The metal orbitals of M_6 interact strongly with each other, creating relatively wide s and d bands. Some of the M_6 framework levels are M-M bonding, some nonbonding, and some antibonding. Thus, the hydrogen atom mainly interacts with some of the low-lying M-M bonding levels to give filled M-H bonding and mostly empty antibonding combinations and a strong hydrogen-to-metal bond is developed with both Ni and Ti atoms in HM_6. The interaction of hydrogen with bonding combinations of the metal orbitals results in a delocalization of the charge in these orbitals into metal-to-hydrogen bonds, and hence a loss of metal-to-metal bonding.

We proceed now to explore the interaction of hydrogen 1s orbital with the metal bands in the 3D NiTiH solid. The addition of an H atom at the center of the metal octahedron described earlier pushes the metal states slightly up in energy, but also takes away from the host lattice one electron. These two effects almost cancel each other. Thus, the Fermi level remains at the same position (raised by about 0.04 eV, see Figure 7) upon the addition of the interstitial H. We can trace the validity of the perturbation theory based characterization of the primary interactions by examining the consequences of interaction in the DOS curves in Figure 7. Projection of the hydrogen 1s orbital is represented by dotted lines and the position of this orbital in the isolated hydrogen by an arrow. As expected, the energy of the hydrogen 1s orbital changes significantly upon interaction with the metal orbitals. We observe the presence of a structure at low energy, centered at about −14.8 eV, which results from the metal-hydrogen bonding. The 1s band is pulled down to a lower energy by ~1.2 eV. The large shift of this band relative to the 1s orbital (−13.6 eV) of the isolated hydrogen is a clear indication of

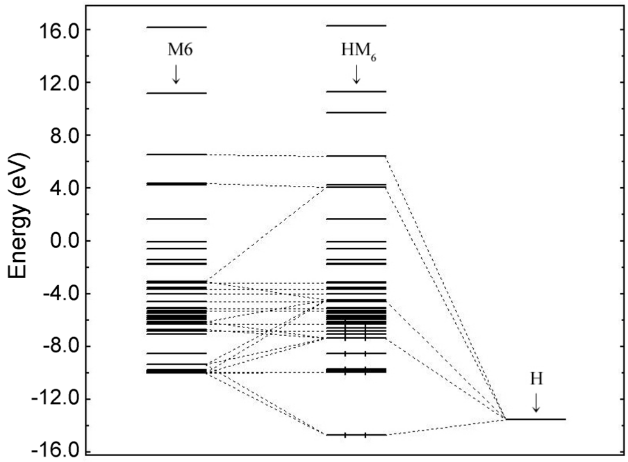


Figure 6. Schematic interaction diagram for HM_6 cluster (Scheme 1) built from the crystal structure of NiTiH.

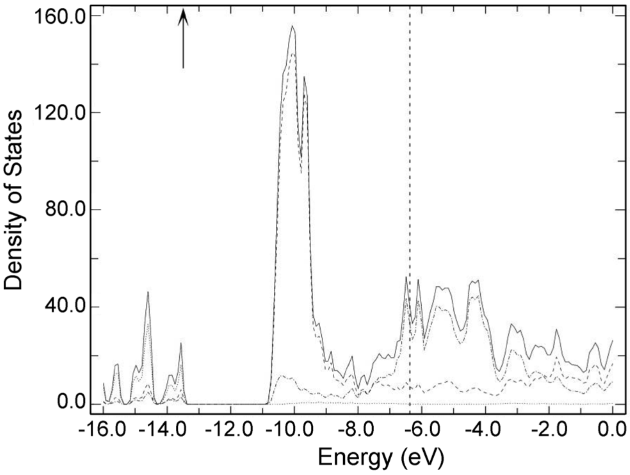


Figure 7. DOS curves for the NiTiH structure: total DOS (solid line), projected DOS on H (dotted line), Ni (dashed line), and Ti (dash-dot line). The arrow indicates the H 1s energy before interaction.

its strong interaction with the metal. It is interesting to note that the Ni d contribution is larger than the Ti d contribution in the low-lying structure of the DOS; the larger interaction of H 1s with nickel states is due to the energy position of H 1s closer to the Ni d than to the Ti d band. The interaction, of course, depends on the shorter Ni-H distances. The DOS curves in Figure 7 are calculated for the choice of the M-H distance in Table 2. Figure 7 looks similar to that of the NiTi lattice without H (Figure 4), except for the 1s band. The orbitals at the bottom of a metal band are metal-metal bonding, those in the middle nonbonding, and those at the top antibonding. What we can say is that 1s interacts more strongly with the bottom of the metal d band than with the top, judging by the interaction diagram in Figure 6. In analogy to discrete complexes we focus our attention on locally strong σ interactions. In addition to d, s orbitals have the proper local symmetry to interact. 1s does not interact with a given level but interacts more (or less) with such and such part of a band. 1s is pushed down in energy and its bonding partners in the metal d band region are characterized by weak Ni-H antibonding and Ti-H nonbonding. This is shown in Figure 7, along with the COOP curves of Figure 8. The three DOS peaks in the region of –13.5 to –16 eV are made up mostly of hydrogen 1s states which are stabilized by interaction with the bonding orbitals of metal d and s.

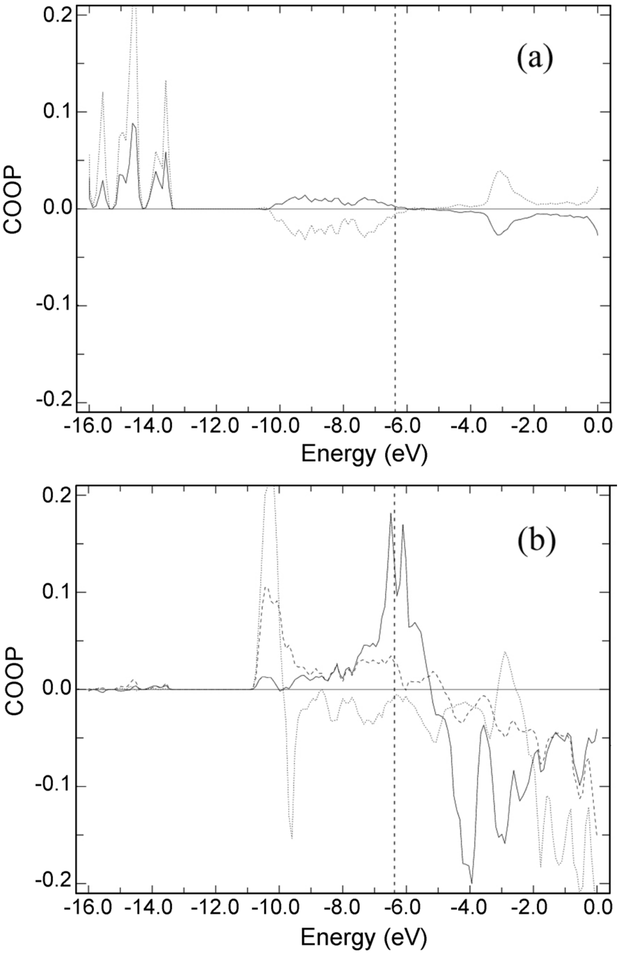


Figure 8. COOP curves for the NiTiH structure: (a) Ti-H (solid line) and Ni-H (dotted line); (b) Ti-Ti (solid line), Ni-Ni (dotted line), and Ni-Ti (dashed line).

This is attested to by the contribution of these orbitals (see projections in Figure 7) and their predominant metal-hydrogen and metal-metal bonding character (see the COOP curves in Figure 8). The antibonding component of the metal-hydrogen interaction spreads over a relatively wide energy range, but the strong one appears at the range of about 1 to 15 eV which is not shown in this figure. Many of the states in it are pushed up above the Fermi level. The COOP curve shows a highly delocalized antibonding region of Ni-H from –10 to –6 eV and Ti-H from −4 to 1 eV. The still higher energy M-H antibonding region arises from out-of-phase mixing of metal s and p with hydrogen 1s. The hydrogen is bound to the metal primarily by the 1s-d, s interaction. It is clear that the 1s bonding state is fully occupied and its antibonding combination is mostly unoccupied. Note that this brings the H atom closer to H^-. The 1s band is substantially more than half populated, with 1.53 electrons per hydrogen atom (see Table 3). Interaction of hydrogen with unfilled metal band states might reverse charge transfer to metal. But the calculations show no signs of that interaction that is not very effective, since the separation in energy between the interacting orbitals is large. The states around the Fermi level contribute invariably to strong Ti-Ti bonding. Whereas the 3d states of nickel are located in a sharp peaks around –10 eV, those of Ti are extended broadly from *ca*. –7 eV up to well above the Fermi level of –3 eV. It is concluded that Ni d orbitals are more or less completely filled and the H 1s states are substantially populated, whereas the Ti d states are partly occupied.

We now turn to the metal-metal bonding changes upon absorption of the hydrogen atoms, as measured by the overlap population. The overlap population of electrons between atoms is a measure of the strength of the covalent bond between them. We find in Table 3 that as the new M-H bond is formed the metal-metal bonds around the binding site are weakened. Thus, the average overlap population (OP) between Ni and Ti drops from 0.204 in the pure NiTi alloy to 0.160 in the NiTi hydride (similarly for Ni-Ni and Ti-Ti the values are 0.026 and 0.004, 0.171 and 0.126, respectively). Thus the hydrogen-metal interactions greatly modify the bond strengths between Ti atoms or between Ti and Ni atoms, all of which neighbor on the hydrogen atom. To some extent the new M-H bond (with the respective OP values of 0.102 and 0.103 for Ni-H and Ti-H) is formed at the expense of weakening the M-M bonds within the metal lattice. These are competing effects. Table 3 summarizes the electron densities, charges, and overlap populations for selected atoms.

Further insight into the bonding mechanism is provided by analyzing the charge distributions. The ionicities of Ti atoms are always positive, whereas those of H and Ni atoms are always negative. This is reasonable since Ti is the more electropositive element than H and Ni. The hydrogen is calculated to be strongly negative with a charge of –0.53. Thus, upon absorption strong electron transfer from both metals to H takes place, and hence the Ti atom becomes more positively (0.65-1.68) and Ni less negatively charged (−0.77). In the Ti case the d band is higher in energy than that of Ni and should interact less effectively with H 1s by the energy criterion of eq. (1) and lose more electrons. The electron transfer derives primarily from the large occupation of 1s on H absorption, and that in turn is a consequence of the bonding interaction of H 1s with the metal-metal bonding states near the bottom of Ni d band, the small peaks in the DOS at the region of –13.5 to –16 eV. Both Ni and Ti metals actually lose their electron densities through this interaction, as many d-1s antibonding combinations are pushed above the Fermi level. These results clearly indicate that the weakening of metal-metal bonds in NiTiH is caused by the electron transfer from metal-metal bonding orbitals to hydrogen.

For hydrogen concentrations larger than 1, up to the structurally investigated material $NiTiH_{1.4}$,[6] the H2 sites are being populated substantially and this site occupancy can no longer be ignored. The small occupancy of the H2 sites and the consequent displacements of the metal atoms could result in some small distortion of the metal d bands and in some small shifts of the low energy metal-hydrogen bonding states. However, the important results of the present calculation are not expected to be significantly altered.

Conclusions

According to our calculations, the H absorption is a favorable process in NiTi alloy structure. The H-metal interaction is favored at the octahedral H1 interstitial site. The Ti-Ti and Ti-Ni bonds neighboring on H are significantly weakened while H-Ti and H-Ni bonds are developed. A substantial charge transfer from bonding states of metal orbitals to hydrogen plays an important role in the creation of the hydrogen-metal bonds, leading to a weakening of metal-to-metal bonds. The overlap population between metal atoms is considerably smaller in the hydride than in pure NiTi. The metal-hydrogen bonding interactions are crucial to the stability of the hydride.

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