SELF–CONSISTENT TOTAL ENERGIES AND ELECTRONIC STRUCTURES OF HYDROGENIZED Ni, Al AND Ni₃Al

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By use of the self–consistent method of linear muffin–tin orbitals with the atomic sphere approximation on the basis of density functional theory, the total energies and the electronic structures of Ni, Al, and their hydrides NiH, AlH and Ni₃AlH are calculated. The theoretical excess energies and the lattice strains due to hydrogen absorption consequently obtained from the ab initio results indicate that Ni is a better hydrogen absorber than Al, and the absorptivity of Ni₃Al dramatically decreases owing to the repulsion between Al and H On the other hand, the changes of band structures due to hydrogenation are found to be remarkable except that for Al, and they are shown to be the qualitative manifestation of existing conclusions from photoemission experiments.

KEY WORDS *total energy, electronic structure, hydrogenized Ni, Ai, Ni₃Al*

Hydrogen in metals and alloys has been massively studied with the increase in both scientific and industrial applications [1]. Among the applications, we would like to outline two impressive ones, one being the rapidly–developed hydrogen–storage alloys, the other the possibility of cold fusion in the medium of transition metals. The first one has given birth to the nickel–metal hydride (Ni–MH) batteries. The negative electrodes made of the hydrogen storage alloys take advantages over the conventional Ni–Cd batteries because of their high energy capacities and low level of Cd pollutants [2]. The second one appears to provide a feasible way of the realization of cold fusion. It is speculated that cold fusion might occur when the density of deuterons inside the palladium crystal becomes sufficently high [3]. Evidently, both the above examples are significant and necessitate more theoretical investigations in the light of electronic structures [4]. This paper is dedicated to the understanding of the effects of hydrogen absorption on the total energies and the electronic structures of nickel, aluminium and their ordered alloy Ni₃Al. The intermetallic compound Ni₃Al is believed to be one of the most important structural materials. A number of good preformances such as the high melting point, the low density and the resistance to oxidation make it sound like an attractive candidate of research [5].

In this work, we use the self–consistent (SC) method of linear muffin–tin orbitals with atomic–sphere approximation (ASA–LMTO) [6,7] in the formalism of density function theory (DFT) [8,9] to calculate the total energies and the electronic structures of the two metals Ni, Al with fcc structures, the ordered $L1_2$ superstructure Ni₃Al and the β–phase hydrides NiH, AlH, and a low H concentration hydride Ni₃AlH. The calculated equilibrium lattice constants are all in good agreement with available experimental data. Those of lthe hydrides are found to increase with the absorption of hydrogen atoms. The lattice strain of Ni due to hydrogenation is also in good agreement with experimental estimate. From the *ab initio* results of absorption energies and lattice strains, it is concluded that Al is harmful to the hydrogen–storage materials. For the structure of Ni₃Al, there are two kinds of octahedral interstitial sites. One is the center

of the octagon cage formed by the six nearest neighbor Ni atoms, the other is the center of the octagon cage formed by four Ni atoms and two Al atoms. Our calculations show that the former place is more stable for a hydrogen atom to stay in. Band-structure results indicate that in Ni_3AlH, the ionicities of Ni atomic spheres are negative, whereas those of H and Al atomic spheres are positive. So, the cations of H are easily captured into the former kind of cages. On the contrary, since they are repellent to aluminium captions, we have less probability to find them in the latter kind of cages. The information given by the electronic structures may be helpful in understanding the hydrogen diffusion in the intermetallic compounds.

The results for hydrides are identical with those for deuterides, because the electronic structure calculations are based on the groundwork of Born-Oppenheimer approximation where the masses of nuclei are regarded as infinite and so there is no difference between the electronic structures of NiH, AlH and those of NiD, AlD.

1. ASA−LMTO Method

The LMTO method has become very fashionable in the past decade because of its excellent accuracy and applicability even to a personal computer. Among the existing LMTO methods, the ASA−LMTO is the least time-consuming one, and it is found to be a very precise approach for the close-packed structures [10] . The ASA is based on two basic assumptions, one being that the kinetic energy of the partial wave tails of muffin-tin orbitals can be fixed independently of energy, the other that the Wigner-Seitz polyhedron can be approximated by an atomic sphere which is namely regarded as the muffin-tin sphere. The cancellation of potential function $P_l(E)(r/S)^l$ with the tails of muffin-tin orbitals from other atomic spheres is required, hence we only need to integrate the radial Schrödinger equation out to the boundaries of atomic spheres.

Within the framework of DFT, the total energy functional per unit cell can be formulated as

$$\langle \Phi|H|\Phi \rangle = \langle \Phi_s|T|\Phi_s \rangle_{ASA} + \frac{1}{2}\sum_{q,q'} Z_t^{eff} Z_{t'}^{eff} e^2 \frac{S_{qq'}}{S}$$
$$+ \sum_q \int_0^{R_t} [\frac{1}{2} V_H(r) - \frac{Z_t e^2}{r} + \in_x (n_t(r))] n_t(r) d^3 r \qquad (1)$$

where the subscrit t, t' denote the species of atoms and q, q' the positions. R_t is the radius of the atomic sphere of type t atom. the first term is the kinetic energy evaluated in the ASA framework. $S_{qq'}$ is a structure constant

$$S_{qq'} = \sum_R \frac{S}{|\vec{R} + \vec{q} - \vec{q'}|} \qquad (2)$$

with S referring to the mean radius of atomic sphere. $V_H(r)$ is the Hartree potential

$$V_H(r) = \int_0^{R_t} \frac{n_t(r')e^2}{|\vec{r} - \vec{r'}|} d^3 r' \qquad (3)$$

Z_t^{eff} is the effective net charge of the atomic sphere, defined as

$$Z_i^{eff} = Z_i - \int_0^{R_i} n_i(r)d^3r \tag{4}$$

$\epsilon_{xc}(n_t(r))$ is the local exchange-correlation energy density of Hedin-Lundqvist [11].

The self-consistent procedure then turns to the solution of the one-electron Schrodinger equation inside the type t sphere at an inequivalent location q in the unit cell

$$[-\frac{h^2}{2m}\nabla^2 + V_t(r)]\Psi_j(r,k) = E_j(k)\Psi_j(r,k) \tag{5}$$

where $V_t(r)$ is the effective one-electron potential

$$V_t(r) = V_H(r) - \frac{Z_t e^2}{r} + \sum_q Z_q^{eff}e^2\frac{S_{qq'}}{S} + V_{xc}(n_t(r)) \tag{6}$$

With $V_{xc}(r)$ denoting the exchange-correlation potential of Hedin-Lundqvist [11], the solution of Eq.(5) is based on the space spanned by the muffin-tin orbitals.The local electron density is then given by the summation over the occupied states of energy band

$$n(r) = \sum_j^{occ.} |\Psi_j(k,r)|^2 \tag{7}$$

The kinetic energy of the non-interacting system in Eq.(1) is then given as

$$\langle \Phi_s|T|\Phi_s\rangle_{ASA} = \sum_j^{occ.} E_j(k) - \sum_q \int_0^{R_t} V_t(r)D^3r \tag{8}$$

2. Calculations and Discussion

The location of H in metals and alloys, as well as metallic glasses has been extensively studied [1,12]. As a result of these studies it is now well established that in fcc metals H prefers to occupying octahedral interstitial sites while in bcc and hcp metals as well as some metallic glasses it tends to occupy tetrahedral sites. Therefore for Ni, Al with fcc structures and Ni_3Al with $L1_2$ structure, only those phases of hydrides in which hydrogen atoms occupy octahedral positions are needed to be considered. As the representative hydrides, the β-phase NiH and selected to be calculated. While in the structure of Ni_3Al, two distinct octahedral interstitial sites accommodate H, each representing a candidate structure. All the above-mentioned structures are illustrated in Fig.1. For calculations concerned with two or more than two kinds of atom, the radii of different atomic spheres are determined by assuming that their ratios are directly the ratios of the corresponding atomic radii.

In the band structure calculations, the $3d^84s^2$ electrons of Ni, the $3s^23p^1$ electrons of Al and the $1s^1$ electron of H are taken as the valence electrons. In practice, only s, p, d orbitals are included to span the subspace. For Ni, Al and H, the electron configurations are assumed to be 4s4p3d, 3s3p3d and 1s2p3d, respectively. The potential parameters of 4p(Ni), 3d(Al) and 2p3d(H) are taken as positive, since they are unoccupied in the free states. In particular, the potential parameters for 2p3d(H) should be far above the upper energy window, because the electrons inside the hydrogen atomic sphere are unlikely to occupy those orbitals. The potential parameters for the rest partial waves are near the energy levels of the corresponding ones in the free states. The special-point technique for Brillouin zone summation is adopted in the
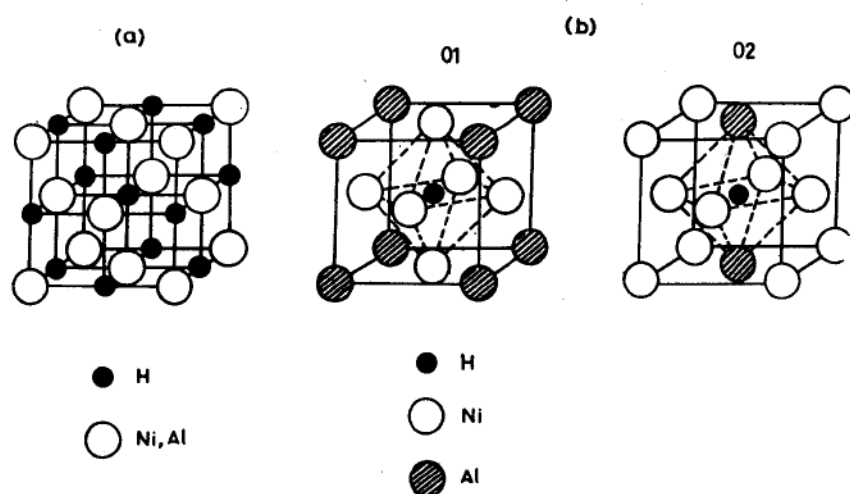
Fig.1 Rocksalt structure of NiH and AlH(a); structures of $Ni_3AlH(O1)$ and $Ni_3AlH(O2)(b)$

calculations so as to accelerate the convergence of charge density [13] . In the calculations of total energies, we take 10 special points in the irreduciable Brillouin zone for Ni, Al and NiH, AlH, and 20 points for Ni_3Al, Ni_3AlH. In some case, 60 or 120 points are involved to get more accurate state densities. The increase of special points does not influence on the results of total energies, because each special point is precisely weighted.

The stoichiometric alloy Ni_3AlH possesses two inequivalent interstitial octahedral sites. One is the position surrounded by six Ni atoms, it is labelled as O1 position.The other is that coordinated by four Ni atoms and two Al atoms, it is labelled as O2 position. We have to at first decide what structure looks more possible. For this purpose, the difference of total energies and electronic structure parameters are calculated at the experimental lattice constant of Ni_3Al (0.3567nm) [14] and shown in Table 1.

Table 1 Comparison of total energies and electronic structure parameters of $Ni_3AlH(O1)$ and $Ni_3AlH(O2)(Ryd \cdot cell)$ [1]

System	E_{tot} Rydeberg	E_F Rydeberg	IDOS(E_F) Al (Ryd · cell) [1]	IDOS(E_F) H (Red · cell) [1]	IDOS(E_F) Ni (Ryd · cell) [1]
$Ni_3AlH(O1)$	−9594.937	−0.0356	2.578	0.208	10.405
$Ni_3AlH(O2)$	−9594.850	−0.0774	2.784	0.213	10.334

The tabulated results reveal that the absorption energy of H to the O1 site is less than that to the O2 site. Hydrogen prefers staying at the O1 sites to locating at the O2 sites. When a hydrogen atom is activated from an O1 site to an O2 site, it has to overcome an energy barrier with height of $\Delta = 1.183eV$. This energy barier is mainly contributed by the static Coulomb interactions between ionized atoms. Both the Al atoms and the H atoms donate their electrons to the Ni atoms, and this results in the repulsion between ion Al and ion H and furthermore hampers the hydrogenation. One can see that the ionicities of the atomic spheres are weakened

when the O1 phase transits into O2 phase. This redistribution of effective charges is to lower down the energy barrier between the O1 phase and the O2 phase. In the following calculation, it is reasonable to select the O1 phase as the ground state of the stoichiometric compound Ni₃AlH.

We have calculated the total energies in relation to lattice constants in the vicinities of equilibrium lattice constants. In order to get the equilibrium lattice constants and the bulk moduli, we process the data with a least–square regression of six–order polynomial. It is found that the calculated equilibrium lattice constants are in agreement with experimental data in the case when they are available [15] (see Tab.2). The predicted bulk moduli are all greater than the experimental data [16]. For Ni₃Al the prediction of bulk modulus is greater than both those for Ni and Al. The hydrogenization reduces the elasticity of Ni₃Al but surprisingly enhances those of Ni and Al.

Table 2   Ab initio results of equilibrium lattice constants, and the bulk
moduli of Ni, Al, Ni₃Al and NiH, AlH, Ni₃AlH

System	Ni	Al	Ni₃Al	NiH	AlH	Ni₃AlH
a_c(theo.).nm.	0.3498	0.3907	0.3523	0.3854	0.4517	0.3613
(exp.).nm.	0.352	0.405	0.3567			
B(theo.).10⁴J / cm³	2.067	1.177	2.456	3.405	5.366	2.178
(exp.)10⁴J / cm³	1.86	0.76	1.804			

Table 3 Electronic structure parameters and charge transfers ΔQ of Ni, Al, Ni₃Al and NiH, AlH, Ni₃AlH at zero temperature and under zero pressure

		Ni	Al	Ni₃Al	NiH	AlH	Ni₃AlH
E_F.Rydberg		−0.075	0.0017	−0.026	−0.251	−0.210	−0.057
IDOS(E_F).	Ni s	0.651	———	0.662	0.625	———	0.664
(Ryd · cell)⁻¹	p	0.745	———	0.809	1.027	———	0.901
	d	8.604	———	8.660	9.147	———	8.844
	Al s	———	1.048	0.908	———	1.275	0.902
	p	———	1.507	1.261	———	1.728	1.238
	d	———	0.445	0.436	———	0.734	0.426
	H s	———	———	———	0.195	0.257	0.204
	p	———	———	———	0.005	0.006	0.005
	d	———	———	———	0.000	0.000	0.000
ΔQ. e	Ni	———	———	−0.132	−0.800	———	−0.408
	Al	———	———	0.395	———	−0.737	0.434
	H	———	———	———	0.800	0.737	0.791

The integrated DOSs(IDOSs) of the s, p, d partial waves at the Fermi energies are listed in Table 3. The total IDOS of each atom is the sum of all the partial IDOs. The effective charges of the atomic spheres due to charge transfer are also listed in Table 3.

The ab initio curves of total energies vs lattice constants and the overall information of electronic structures are depicted in Figs.2–7.

The absorption energy of hydrogen is defined to be the difference between the total ground–state energies of the metals or alloys and those of their hydrides minus the ground–state
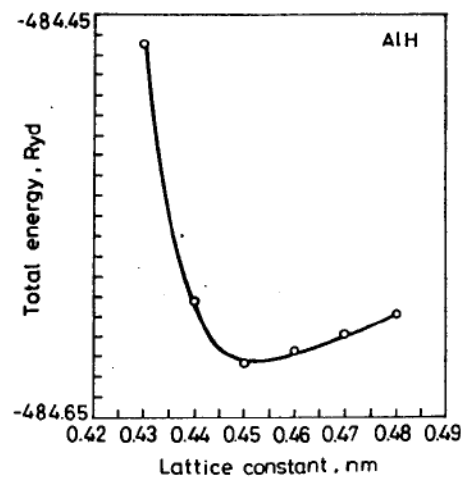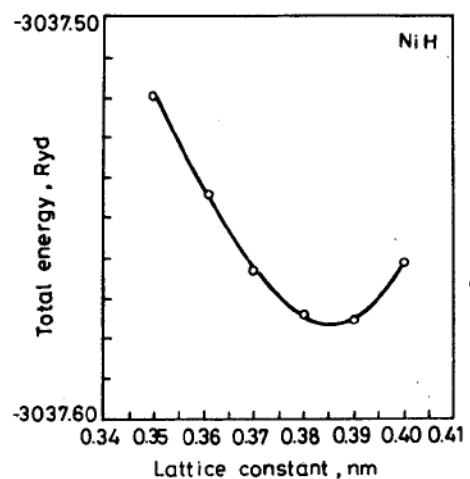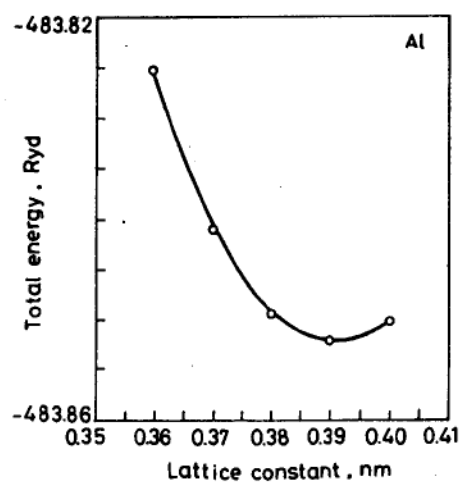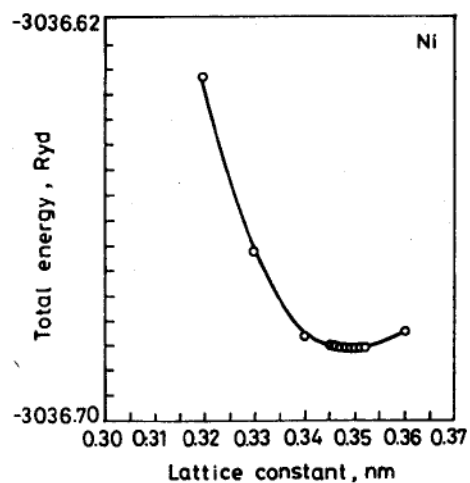
Fig.2 Total energies vs lattice constants for Ni and NiH

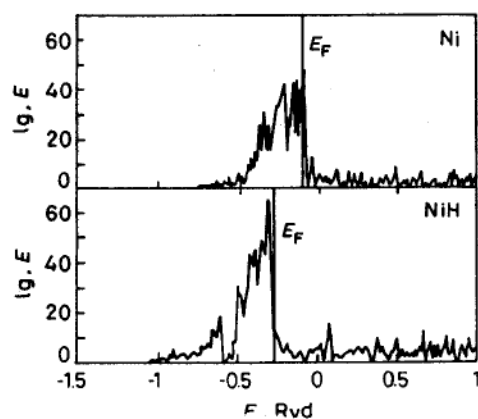Fig.4 Total energies vs lattice constants for Al and AlH

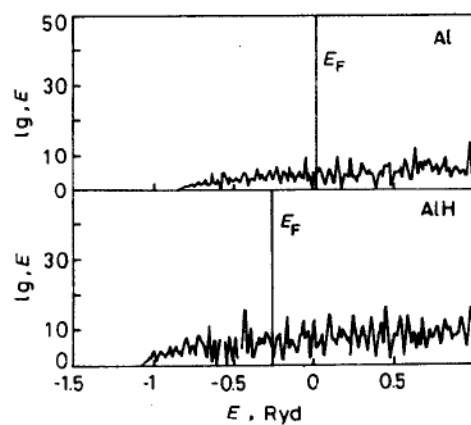Fig.3 Electronic DOSs and Fermi energies of Ni and NiH at equilibrium

Fig.5 Electronic DOSs and Fermi energies of Al and AlH at equilibrium
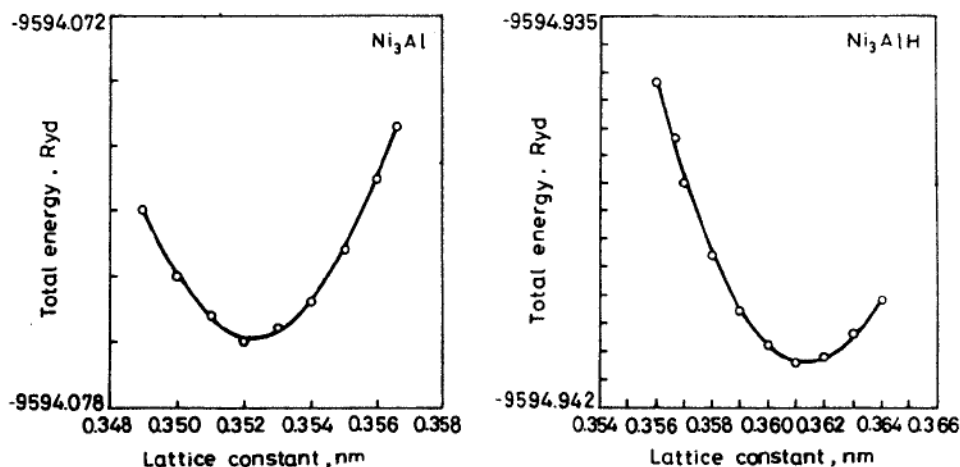
Fig.6 Total energies vs lattice constants of Ni₃Al and Ni₃AlH(O1)

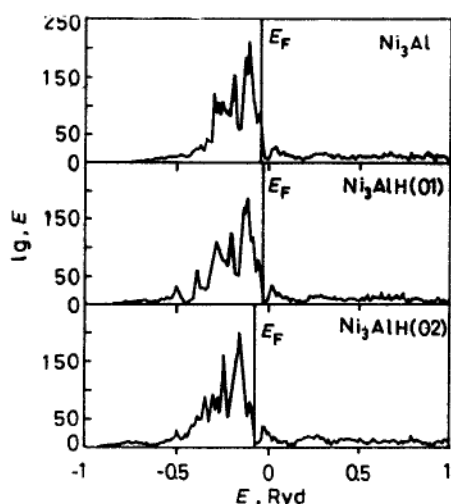Fig.7 Comparison of electronic DOSs and Fermi energies of Ni₃Al, Ni₃AlH(O1) and Ni₃AlH(O2) with the same lattice constants

energy of a free-state hydrogen atom (namely 13.6eV)

$$E_{abs}(MH_x, a_e) = E_{tot}(MH_x, a_e^{MH_x})$$
$$- E_{tot}(M, a_e^M) - x E_{tot}(H) \qquad (9)$$

The volume expansion due to hydrogen absorption is

$$\frac{\Delta\Omega}{\Omega} = 3 \times \frac{a_e^{MH_x} - a_e^M}{a_e^M} \qquad (10)$$

The absorption energies and the lattice strains of the hydrides studied are illustrated in Tab.4. The theoretical lattice expansion of Ni is in good agreement with the experimental value 0.28 measured by Bauer et al.using X-ray diffuse scattering technique [1]. The data in Tab.4 demonstrates the overall conclusion that group IIIA elements such as aluminium and boron are no good for hydrogen storage. The lattice expansion and the absorption energy of AlH is much greater than those of NiH. On the other hand, for the intermetallic compound Ni₃Al, the absorption of hydrogen to the O1 interstitial sites leads to a small volume expansion but heeds more energy than the formation energy of NiH.

Table 4 The calculated hydrogen-absorption energies and the lattice strains of NiH, AlH and Ni₃AlH(O1)

System	Ni₃AlH	NiH	AlH
E_{abs}, eV / atom	1.847	1.500	3.191
$\Delta\Omega / \Omega$	0.077	0.305	0.468

The plots of state densities represent general features of electronic structure change attributed to hydrogen addition. They are, the lowering of filled states and for Ni and Ni_3Al the growth of low-energy peaks below the apogees of d-bands. For other well-studied transition-metals such as Pd, the above features have been manifested by photoemission experiments. The projected DOSs (PDOSs) at Fermi energies notably decrease after hydrogenization except that of aluminium hydride (see Tab.5). As a result, the electronic specific heat γ and the Pauli paramagnetic susceptibility χ_P are remarkably reduced, since they are directly proportional to the state density at Fermi energy. This is in general agreement with the experimental conclusion that the addition of H to transition metals and alloys decreases γ and χ_p[1]. Further, it has been pointed out that the state densities of metallic hydrides affect directly the Mossbaur parameters particularly in the study of isomer shifts and magnetic hyperfine interactions[1]. Moreover, our results show that the mentioned electronic properties do not alter much in the case of the hydrogenization of Al.

Table 5 The projected DOSs at Fermi energies of Ni, Al, Ni_3Al and NiH, AlH, Ni_3AlH at equilibrium. The state densities are in (Ray · cell)[1]

		Ni	Al	Ni_3Al	NiH	AlH	Ni_3AlH
IDOS(E_f),	Ni s	0.988	———	0.232	0.944	———	0.018
$(Ryd \cdot cell)^{-1}$	p	1.462	———	1.265	1.830	———	0.308
	d	56.985	———	25.170	25.166	———	2.450
	Al s	———	2.507	0.712	———	4.159	0.166
	p	———	11.892	0.686	———	9.313	0.244
	d	———	7.103	0.590	———	5.623	0.127
	H s	———	———	———	0.129	0.740	0.008
	p	———	———	———	0.009	0.048	0.001
	d	———	———	———	0.000	0.001	0.000
Total	Ni	59.434	———	26.667	27.941	———	2.777
$(Ryd \cdot cell)^{-1}$	Al	———	21.503	1.987	———	19.095	0.010
	H	———	———	———	0.201	0.759	0.517

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