

## Research Article

# First Principles Study of Electronic Structure and Magnetic Properties of TMH (TM = Cr, Mn, Fe, Co)

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First principles calculations are performed using a tight-binding linear muffin-tin orbital (TB-LMTO) method with local density approximation (LDA) and atomic sphere approximation (ASA) to understand the electronic properties of transition metal hydrides (TMH) (TM = Cr, Mn, Fe, Co). The structural property, electronic structure, and magnetic properties are investigated. A pressure induced structural phase transition from cubic to hexagonal phase is predicted at the pressures of 50 GPa for CrH and 23 GPa for CoH. Also, magnetic phase transition is observed in FeH and CoH at the pressures of 10 GPa and 180 GPa, respectively.

## 1. Introduction

Metal hydrides have been attracting attention of scientists for decades. Their physical properties are interesting from both fundamental and practical points of view. Many transition metals react readily with hydrogen to form stable metal hydrides [1]. Metal hydrides are of intense scientific and technological interest in the view of their potential application, for example, for hydrogen storage, in fuel cells and internal combustion engines, as electrodes for rechargeable batteries, and in energy conversion devices. Hydrides for hydrogen storage need to be able to form hydrides with a high hydrogen to metal mass ratio but should not be too stable, so that the hydrogen can easily be released without excessive heating [2]. Among those, the metal hydrides are of particular interest due to their application in hydrogen storage for fuel cells [3, 4]. The physical properties of metal hydrides are quite interesting from the practical point of view. For example, the density of hydrogen in metal hydrides is larger than that in liquid hydrogen [5]. Previously the first principles calculations were performed for metal dihydrides with the fluorite structure [6, 7]. The stability and electronic structure of the transition-metal hydrides were reported [8]. Phase

transformations, crystal and magnetic structures of highpressure hydrides of d-metals were analyzed by Antonov [9].  $\gamma$ -CrH and  $\varepsilon$ -CrH hydrides were prepared electrolytically and studied by neutron diffraction and inelastic neutron scattering at liquid helium temperatures [10]. Previously we have investigated the pressure induced magnetic phase transition in hexagonal FeH and CoH [11].

In this work, the structural, electronic, and magnetic properties of 3d transition metal hydrides (CrH, MnH, FeH, CoH) are investigated using TB-LMTO method. The weight percentage of hydrogen in Cr, Mn, Fe, and Co is also calculated.

## 2. Computational Details

The TB-LMTO (tight-binding linear muffin-tin orbital) method has been used [12, 13] to compute the electronic structure and the basic ground state properties of TMH. In the LMTO scheme, the crystal potential is approximated by a series of nonoverlapping atomic like spherical potentials and a constant potential between the spheres. The Schrödinger equation can be solved in both regions. These solutions are

then matched at the sphere boundaries to produce muffintin orbitals. These muffin-tin orbitals are used to construct a basis which is energy independent, linear order in energy and rapidly convergent. Each orbital must satisfy Schrödinger's differential equation in the region between the atoms. Here the potential is flat on a scale of 1 Ry and, since the energy range of interest begins near the point where the electron can pass between the atoms and extends upwards by about 1 Ry, it seems natural to choose orbital, which have zero kinetic energy, that is, satisfy the Laplace equation, in the interstitial region. In the tight-binding muffin-tin orbital the solution of Schrödinger's equation is written as follows:

$$\left|\chi^{\alpha}\left(\varepsilon\right)\right\rangle = \begin{cases} \left|\phi\left(E\right)\right\rangle N^{\alpha}\left(E\right) + \left|J^{\alpha}\right\rangle P^{\alpha}\left(E\right) & r \leq w, \\ \left|K^{\alpha}\right\rangle & r \geq w, \end{cases}$$
(1)

where *r* is any distance from the centre of the muffin-tin sphere, *w* is the average Wigner-Seitz radius, and  $\alpha$  are dimensionless screening constants. Inside the MT sphere, the base field or unscreened field  $|K\rangle$  is defined by

$$|K\rangle = |\phi(E)\rangle N^{\alpha}(E) + |J^{\alpha}\rangle P^{\alpha}(E).$$
(2)

In the interstitial region, the screened field  $|k^{\alpha}\rangle$  is defined by

$$\left|k^{\alpha}\right\rangle = \left|\phi\left(E\right)\right\rangle N^{\alpha}\left(E\right) + \left|J^{\alpha}\right\rangle P^{\alpha}\left(E\right) - \left|J^{\alpha}\right\rangle S^{\alpha},\qquad(3)$$

where  $\phi(E)$  is normalized to unity in its sphere.  $J^{\alpha}$  is the screen field radial function and  $S^{\alpha}$  is the screened structure matrix. The elements of the diagonal matrices *P* and *N* are

$$P^{\alpha}(E) = \frac{\{\phi(E), k\}}{\{\phi(E), J^{\alpha}\}} = \frac{P^{o}(E)}{1 - \alpha P^{o}(E)},$$

$$N^{\alpha}(E) = \frac{\{J^{\alpha}, k\}}{\{J^{\alpha}, \phi(E)\}} = \left(\frac{w}{2}\right)^{1/2} \dot{P}^{\alpha}(E)^{1/2}.$$
(4)

The set of energy dependent MTO's  $|\chi^{\alpha}(E)\rangle$  thus equals  $|k^{\alpha}\rangle$  and  $|k\rangle$ ; the linear combination  $|\chi^{\alpha}(E)\rangle u^{\alpha}$ , specified by a column vector  $u^{\alpha}$ , is seen to be a solution of Schrödinger's equation at energy *E* for the MT potential if it equals the one center expansions  $|\phi(E)\rangle > N^{\alpha}(E)u^{\alpha}$  in the spheres, that is, if the set of linear homogeneous equations  $[P^{\alpha}(E) - S^{\alpha}]u^{\alpha} = 0$  has a proper solution. This is the generalization of the so-called tail cancellation or Kerringa-Kohn-Rostoker (KKR) condition.

The secular matrix  $[P^{\alpha}(E) - S^{\alpha}]$  depends on the potential only through the potential functions along the diagonal and for the most localized set it has the TB two-center form with  $S^{\alpha}$  playing the role of the transfer integrals.

The screened field  $|k^0\rangle$  is given by the superposition of bare fields  $|k^0\rangle$  and that the relationship between the bare and screened structure matrices is as follows:

$$S^{\alpha} = S^{o} (1 - S^{o})^{-1}.$$
 (5)

The expansion coefficient  $S^o$  forms a Hermitian matrix which is dimensionless and independent of the scale of the structure. This is the so-called (bare) canonical structure matrix.

The KKR equations have the form of Eigen value problem if  $P^{\alpha}$  is a linear function of *E*. This is true, if  $\alpha = \gamma$  (potential parameter) in this case the effective two-center Hamiltonian is as follows:

$$H_{ij}^{\gamma} = C_i S_{ij} + \left(\sqrt{\Delta_i}\right) S_{ij}^{\gamma} \left(\sqrt{\Delta_i}\right).$$
 (6)

For crystals, where the matrix inversion in (6) can be performed, one may obtain from  $S^{\circ}$  (or)  $S^{\alpha}$ .

To obtain Eigen value when  $\alpha \neq \gamma$ , energy independent orbitals are needed. Now,  $|\chi^{\alpha}(E)\rangle$  is independent of energy; in the interstitial region and in the spheres, its first energy derivative at  $E_{\gamma}$  will vanish. Therefore, the orbital base is as follows:

$$\left|\chi^{\alpha}\right\rangle = \left|\phi\right\rangle + \left|\dot{\phi}^{\alpha}\right\rangle h^{\alpha}.$$
(7)

In this base, the Hamiltonian matrices are

$$\left\langle \chi \left| H - E_{\gamma} \right| \chi \right\rangle = h \left( 1 + oh \right),$$
 (8)

$$(H-E)\left|\phi\left(E\right)\right\rangle = 0\tag{9}$$

 $H - E_{\gamma}$  is the effective two-center TB Hamiltonian. This has a shorter range. Therefore, this set of equations is used in self-consistent calculations. In the interstitial region (8) becomes

$$\left\langle \chi^{\alpha} \left| H - E_{\gamma} \right| \chi^{\alpha} \right\rangle = h^{\alpha} \left( 1 + o^{\alpha} h^{\alpha} \right).$$
 (10)

The set of  $|\chi^{\alpha}\rangle$  is thus complete to first order in  $(E - E_{\gamma})$  and it can yield energy estimates correct to the third order. A Von-Barth and Hedin [12] parameterization scheme has been used for the exchange correlation potential within the local density approximation (LDA). The accuracy of the total energies obtained within the density functional theory, often using LDA, is in many cases sufficient to predict which structure at a given pressure has the lowest free energy [14]. The atomic sphere approximation (ASA) has been used in the present work. The Wigner-Seitz sphere is chosen in such a way that the sphere boundary potential is at its minimum and the charge flow is in accordance with the electronegativity criteria. s, p, and d partial waves are included. The tetrahedron method [15] of the Brillouin zone (k-space) integration has been used to calculate the density of states.

#### 3. Results and Discussion

3.1. Stability of TMH and Formation Energy. At ambient condition, all the metal hydrides TMH (TM = Cr, Mn, Fe, Co) crystallize in fcc structure with the space group Fm3m (225). The Wyckoff positions for each metal and hydrogen are 4a:(0,0,0) and 4b:(0.5,0.5,0.5), respectively, and contain four formula units per unit cell. The stability of these metal hydrides is analyzed by computing the formation energy using the following relation:

$$\Delta H = E_{\text{tot}} (\text{TMH}) - E_{\text{tot}} (\text{TM}) - E_{\text{tot}} (\text{H}), \qquad (11)$$

where  $E_{tot}$  (TMH) is the energy of the primitive cell of TMH.  $E_{tot}$  (TM) and  $E_{tot}$  (H) are the energies of a transition metal atom and a hydrogen atom. The variation of heat of formation for chromium, manganese, iron, and cobalt monohydride with rocksalt structure is shown in Figure 1. It is observed that the stability of the hydride rapidly increases as we move from chromium to iron and the heat of formation of CoH is less than FeH.

Figure 2 offers a further illustration of the importance of the valence electron count for the chemical hydrogen insertion energy. It shows the chemical component of the hydrogen insertion energy as function of the number of valence electrons (s + d) for the hydrides (TMH) in rock salt structure.

3.2. Structural Phase Transition. The total energy calculation is carried out for cubic and hexagonal structures of CrH and CoH for various pressures and the total energy versus reduced volume is plotted in Figure 3. Hexagonal structure with the space group P6<sub>3</sub>/mmc (194) is used for total energy calculation. The Wyckoff positions for each metal and hydrogen are 2a:(0,0,0) and 2b:(0.333,0.667,0.25), respectively, and contain two formula units per unit cell. In order to calculate the transition pressure, the Gibbs free energy is calculated for the two phases using the expression

$$G = E_{\rm tot} + PV - TS. \tag{12}$$

Since the theoretical calculations are performed at 0 K, the Gibbs free energy will become equal to the enthalpy (H)

$$H = E_{\rm tot} + PV. \tag{13}$$

At a given pressure, a stable structure is one in which the enthalpy has its lowest value. The transition pressures are calculated at which the enthalpies of the two phases are equal. The enthalpy versus pressure curves corresponding to the cubic and hexagonal phases of CrH and CoH are shown in Figure 4. It is observed that, at normal and low pressures, the thermodynamically stable phase is cubic structure. A pressure induced structural phase transition from cubic to hexagonal phase is observed at the pressure of 50 GPa for CrH and 23 GPa for CoH.

Metal hydrides represent an exciting way of hydrogen storage which is inherently safer than the compressed-gas or liquid storing. Also, some intermetallics (including metals and alloys) store hydrogen at a higher volume density than liquid hydrogen. Elements, especially those in groups I– IV and some transition metals, have their hydride and amide/imide forms. That has, therefore, still plenty of scope for further exploring metal-H systems for hydrogen storage. In our study, the storage capacity, formation energy per unit volume (Ry.), and weight percentage of hydrogen for chromium, manganese, iron, and cobalt are computed and are given in Table 1. Our results conclude that the hydrogen storage capacity decreases as we move from chromium to cobalt.

3.3. Band Structure. The configurations of Cr  $4s^2$   $3d^4$ , Mn  $4s^2$   $3d^5$ , Fe  $4s^2$   $3d^6$ , Co  $4s^2$   $3d^7$ , and H  $1s^1$  are treated as the valence electrons. The band structure of all above-mentioned

TABLE 1: Weight % of hydrogen in Cr, Mn, Fe, and Co.

	Formation energy/unit volume (Ry.)	Density of H/unit cell	Weight % of hydrogen
CrH	-0.1148	8.7450	1.90
MnH	-0.1033	9.4799	1.80
FeH	-0.0953	9.7968	1.77
СоН	-0.0999	9.7163	1.68

metal hydrides at normal pressure is given in Figure 5. The band structures of CrH and MnH have 4 valence bands corresponding to 7 and 8 valence electrons. FeH and CoH have 5 valence bands corresponding to 9 and 10 valence electrons, respectively. At the bottom, the band structure shows first deep narrow band with low dispersion, which is mainly due to the nonmetal H-1s state. The valence states are separated by a wide gap from the occupied states, indicating covalent behavior. The empty conduction bands are highly overlapping with the valence bands. Above the Fermi level the empty conduction bands are present with a mixed s, p, and d characters. The optimized lattice constants, the equilibrium volume  $V_0$  (Å<sup>3</sup>), valence electron density  $\rho$  (electrons/Å<sup>3</sup>), Fermi energy, density of states at Fermi energy, Wigner-Seitz radius, and band energy of cubic metal hydrides are given in Table 2. Valence electron density (VED) is defined as the total number of valence electrons divided by volume per unit cell which is an important factor for analyzing the super hard materials. It is worth noting that the calculated VEDs for CrH are higher than those of Cr (0.5187) and for MnH, FeH, and CoH are slightly less than those of Mn (0.6644), Fe (0.78), and Co (0.89) metals, respectively, and are comparable to 0.70 electrons/Å<sup>3</sup> for diamond [16].

3.4. Density of States. To understand the correlation between the electronic and mechanical properties, we have computed the density of states under equilibrium geometry. The total DOS of all metal hydrides at normal pressure is shown in Figure 6 and it is observed that the spike near -0.5 Ry. is due to metals hydrogen bonding which is clearly shown in partial DOS (Figure 7). It is observed that the H-1s states are near -0.5 Ry. and they are hybridized with the metal s and p states. The dotted line indicates the Fermi level. The d-state electrons of the metal atoms contribute to majority of the DOS near the Fermi level. This indicates that this 3d state intensively hybridize with the H-2p states. The DOS of M-d and H-p states are energetically degenerated from the top of the valence band, indicating the possibility of covalent bonding between the metal (TM-Cr, Mn, Fe, and Co) and H atom. However, the main hybridization in this energy window concerns with 3d state of metal atom and s state of hydrogen atom.

3.5. Charge Density Analysis. An understanding of the nature of the chemical bond can be aided by the studies of the distribution of charges in real space. The real space charge density can also be used to understand features of



FIGURE 2: Chemical contributions to the hydride formation energy as function of the number of valence electrons (energy given per  $H_2$  molecule).



FIGURE 3: Total energy versus reduced volume for TMH.



FIGURE 4: Enthalpy as a function of pressure.



FIGURE 5: Band structures of cubic TMHs at normal pressure.



FIGURE 6: Total density of states of cubic TMHs at normal pressure.

TABLE 2: Lattice constant  $a_o$  (Å), the equilibrium volume  $V_0$  (Å<sup>3</sup>), valence electron density  $\rho$  (electrons/Å<sup>3</sup>), Fermi energy  $E_F$  (Ry.), density of states at Fermi energy N ( $E_F$ ), Wigner-Seitz radius  $R_{WZ}$  (a.u), and band energy  $E_B$  (Ry).

	CrH	MnH	FeH	СоН
	3.77	3.67	3.63	3.64
$a_o$ (Å)	3.71 <sup>a</sup>	3.62 <sup>a</sup>	3.59 <sup>a</sup>	3.60 <sup>a</sup>
	3.854 <sup>b</sup>			
$V_0$	13.395	12.358	11.958	12.057
ρ	0.5226	0.6474	0.7526	0.8294
$E_F$ (Ry)	0.0881	0.0817	0.0743	0.0256
$N(E_F)$	15.8469	18.8391	26.8858	63.6115
$R_{\rm WZ}$	2.2105	2.1519	2.1284	2.1343
$E_B$	-1.1722	-1.4232	-1.65767	-2.0608

<sup>a</sup>Ref. [8]. <sup>b</sup>Ref. [10], expt.



FIGURE 7: Partial density of states of cubic TMHs at normal pressure.

the electronic properties in a real material. One has to remember that the charge density very much depends on the crystal structure and different characteristics may be formed for one and the same compound in different structural arrangements. The covalent characteristics between metal and H atoms can be confirmed by the charge density distribution. The charge density distribution of TMHs is shown in Figure 8. It is clearly seen that the charge strongly accumulate between the transition metals and hydrogen atoms, which means that a strong directional bonding exist between them. Thus, the covalent characteristics between them can be confirmed by the charge density distribution. The total charge transfer from the transition metals to hydrogen atom has some ionic character. Thus, the bonding may be a mixture of metallic and covalent and ionic attribution.

3.6. Magnetic Phase Transition of FeH and CoH. The magnetic moments of FeH and CoH at normal and various pressures are investigated and are given in Figure 9. It is observed that magnetic moment decreases as the pressure increases and it will become zero at  $V/V_0 = 0.5$  in CoH and at  $V/V_0 = 0.9$  in FeH. It indicates that as pressure increases



FIGURE 8: Charge density plot.



FIGURE 9: Variation of magnetic moment with reduced volume.



FIGURE 10: Spin dependent total density of states of FeH and CoH.

the magnetic property of the metal hydrides decreases. The magnetic to nonmagnetic transition occurs at a pressure of 10 GPa in FeH and 180 GPa in CoH. The main reason behind this magnetic transition is magnetic collapse due to band widening in transition metal ions under pressure. It has been found that the contribution to the magnetic moment is entirely from Fe and Co atoms rather than H atom. The spin dependent total density of states is given in Figure 10. It is found that the highest spike due to 3d state lies slightly above the Fermi level in the minority spin (spin up) whereas in the majority spin (spin down), it lies slightly below the Fermi level.

## 4. Conclusions

The band structure, density of states, magnetic phase transition, and charge density under various pressures are investigated based on first principles calculation under the frame work of tight-binding theory within local density approximation. It is found that a pressure induced structural phase transition from cubic to hexagonal phase is observed at the pressure of 50 GPa for CrH and 23 GPa for CoH. The magnetic to nonmagnetic transition occurs at the pressure of 10 GPa in FeH and 180 GPa in CoH.

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