

## Electronic structure of FeTiH

To cite this article: M Gupta 1982 *J. Phys. F: Met. Phys.* **12** L57

View the [article online](#) for updates and enhancements.

### You may also like

- [Enhancing the photocatalytic degradation of Fe-Ti over SiO<sub>2</sub> nanocomposite material for paraquat removal](#)  
Senee Kruanetr and Ratchaneekom Wanchanthuek
- [Buried-interfacial reactivity of palladium-coated Fe<sub>3</sub>O<sub>4</sub>/FeTi thin films during vacuum or hydrogen annealing](#)  
J H Sanders and B J Tatarchuk
- [Mössbauer study of titanium implanted -Fe](#)  
M Kopcewicz, J Jagielski and A Grabias

## LETTER TO THE EDITOR

# Electronic structure of FeTiH

Michèle Gupta

Le Centre de Mécanique Ondulatoire Appliquée du CNRS, 23, rue de Maroc, 75019 Paris, France

and

L'Université de Paris-Sud, Bâtiment 510, 91405 Orsay, France

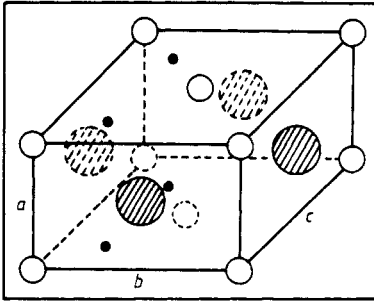
Received 16 November 1981

**Abstract.** We present the results of a band structure study of the electronic properties of  $\beta$  FeTiH. The density of states is characterised by a structure at 9 eV below the Fermi energy, resulting from the metal-hydrogen interaction, and the Fermi energy falls in a rising portion to the density of states; we find 23.93 states of both spin per Ryd FeTiH at the Fermi level. A comparison with the electronic structure of pure FeTi is also given.

In spite of a substantial technological interest in the hydrides of intermetallic compounds as materials for hydrogen storage, chemical heat pumps, electrodes in fuel cells, etc, which has stimulated extensive experimental effort, no theoretical study of their electronic structures has yet been reported. In this letter, we present the most salient features of the first electronic structure study of stoichiometric  $\beta$  FeTiH using an augmented plane wave (APW) band structure calculation. The crystal potential was constructed using Slater's local exchange approximation; the departure from a constant value of the muffin-tin (MT) potential outside the MT spheres was taken into account since this region represents about 50% of the unit cell volume. A detailed report of the work will be presented elsewhere.

The unit cell of FeTiH is shown in figure 1. Structural studies (Thompson *et al* 1978, Fischer *et al* 1978) have been interpreted in terms of an orthorhombic crystal structure which can be viewed as resulting essentially from the doubling of the CsCl unit cell of pure FeTi followed by a large tetragonal distortion due to an expansion along the [110] directions of the CsCl lattice, and a further orthorhombic distortion. The H atoms are located at octahedral sites with two Fe atoms as first neighbours and four Ti atoms as second neighbours; they form strings along the original [110] direction of the CsCl cell of FeTi. Our band structure results can be understood in terms of (i) the folding of the bands of FeTi due to the doubling of the size of the CsCl cell, (ii) the expansion of the unit cell volume and the lifting of the degeneracies due to the orthorhombic distortion, and (iii) the changes brought by the presence of the hydrogen atoms in the lattice.

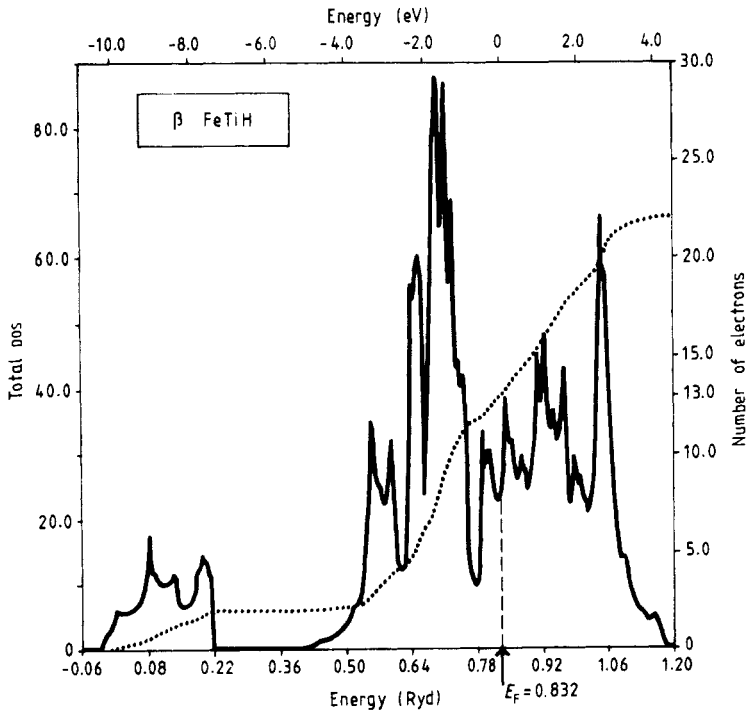
Pure FeTi is isoelectronic to Cr and its Fermi energy  $E_F$  falls in the valley of the density of states (DOS) characteristic of the bcc metals. In figure 2, we have plotted the total DOS of FeTiH. We observe, as in the pure transition metal hydrides (Switendick 1978), the presence of a structure at low energy, centred at about 9 eV below  $E_F$ , which results from the metal-hydrogen bonding. A detailed analysis reveals that the



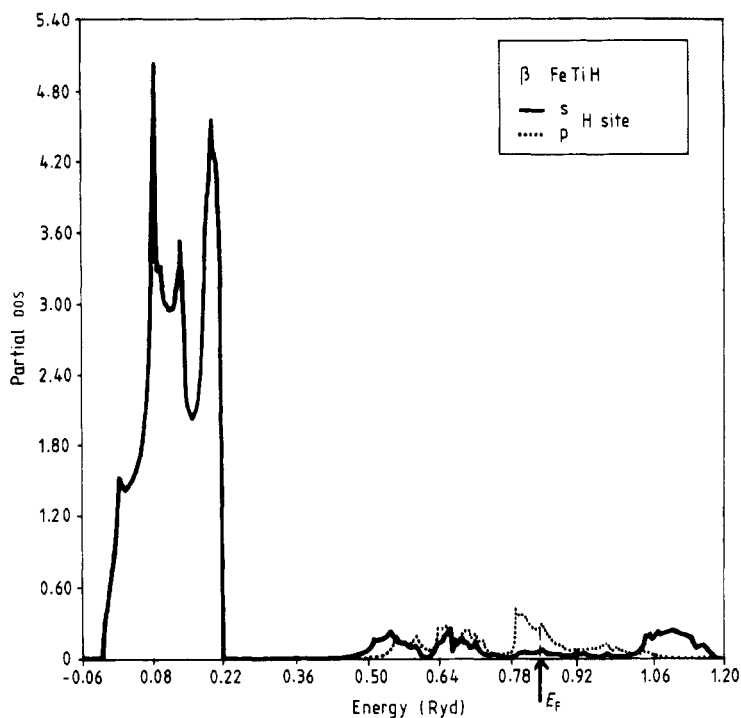
**Figure 1.** The orthorhombic unit cell of  $\beta$  FeTiH (Thompson *et al* 1978, Fischer *et al* 1978).  
 ● H atoms; ○ Fe atoms; ⊗ Ti atoms;  $a = 2.956 \text{ \AA}$ ;  $b = 4.543 \text{ \AA}$ ;  $c = 4.388 \text{ \AA}$ .

metal states which participate in this low-lying structure were previously filled in the pure metal. A partial DOS analysis into its angular momentum components inside the hydrogen and the metal MT spheres is presented in figures 3–5 and shows that the structure at low energy is essentially due to hydrogen s, but also to metal d and, to a lesser extent, metal s and p states. It is interesting to notice that the Fe d contribution is much larger than the Ti d contribution, at low energy.

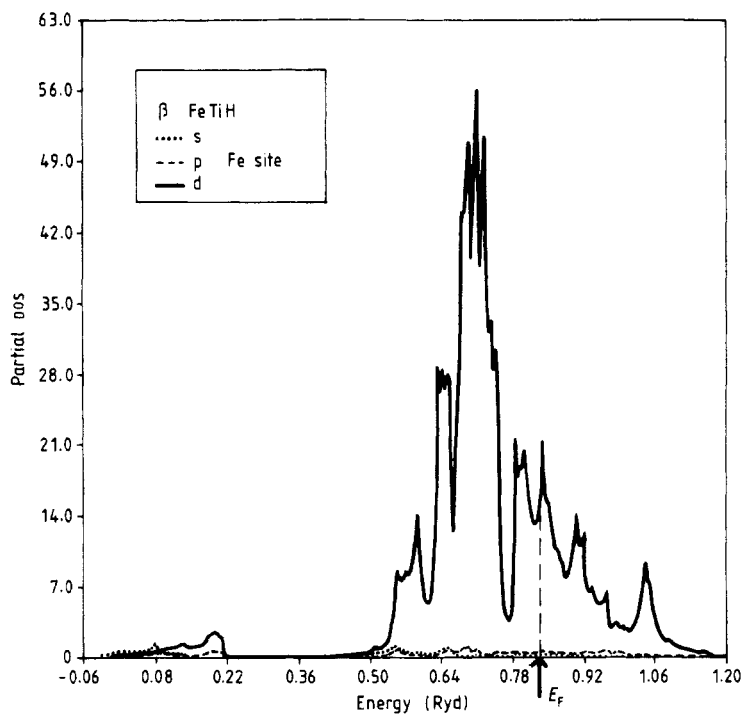
At higher energies, we find the metal d bands in which we observe around  $E = 0.78 \text{ Ryd}$ , the valley characteristic of the bcc metals, which separates the Fe–Ti bonding from the Fe–Ti antibonding manifold. Below the valley, as shown clearly in figures 4 and 5, the metal states have essentially Fe d character, while the Ti d



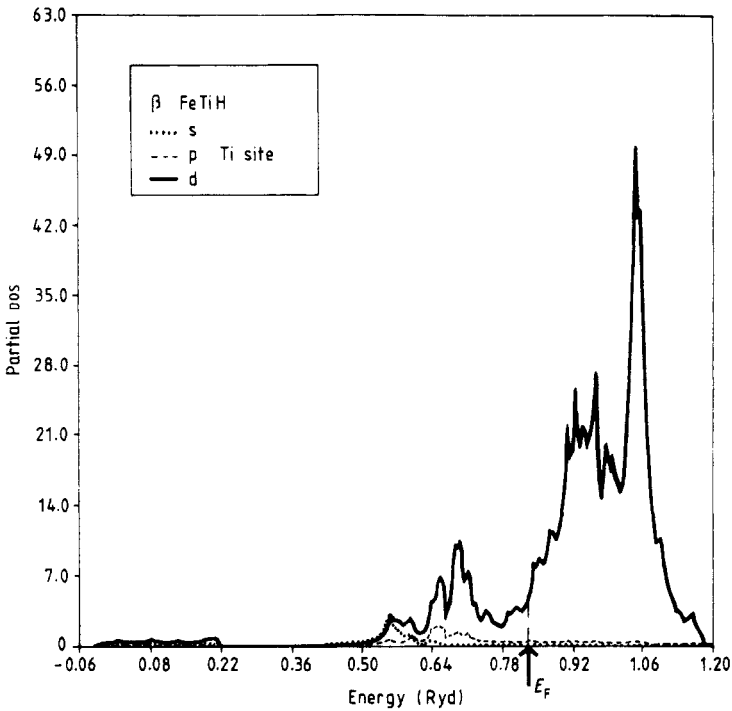
**Figure 2.** The total DOS of  $\beta$  FeTiH (full curve, left-hand side scale). Units are states of both spin per Ryd FeTiH. The total number of electrons (dotted curve, right-hand side scale).



**Figure 3.** The angular momentum DOS analysis  $n_l$  ( $l = 0, l = 1$ ) inside the hydrogen MT sphere  $R_H = 1.0513$  au. Units are states of both spin per Ryd FeTiH.



**Figure 4.** The angular momentum DOS analysis  $n_l$  ( $l = 0, l = 1, l = 2$ ) inside the Fe MT sphere  $R_{Fe} = 1.9155$  au. Units are states of both spin per Ryd FeTiH.



**Figure 5.** The angular momentum DOS analysis  $n_l$  ( $l = 0, l = 1, l = 2$ ) inside the Ti MT sphere  $R_{Ti} = 2.3396$  au. Units are states of both spin per Ryd FeTiH.

contribution is overwhelming at higher energies. This feature, which is reminiscent of the relative position of the atomic d levels is also encountered in pure FeTi (Yamashita and Asano 1972, Papaconstantopoulos 1975). From an analysis of the metal states which are modified by the metal-hydrogen interaction, we found that a full branch of metal p states, which in pure FeTi lies at more than 1 eV above  $E_F$ —namely, the  $M'_5$  point of the cubic Brillouin zone (BZ) of the CsCl structure—is lowered by about 3.4 eV and falls below  $E_F$  in the metal d bands of the hydride. As observed for transition metal hydrides (Switendick 1978 and references therein, Gupta 1979), the metal states having an s symmetry at the hydrogen site are strongly scattered by the H potential which is characterised by large s phase shifts. The lowering of empty metal states by the hydrogen potential certainly plays a role in the stability of the hydride and also controls the position of the Fermi energy. As shown in figure 2, the Fermi level is shifted to higher energies from pure FeTi to the hydride since, for the latter, it falls above the valley of the DOS. Thus, the model proposed by Hempelmann *et al* (1978) is qualitatively correct. Nevertheless, as discussed above, due to the lowering of empty metal states by the metal-hydrogen interaction, less than one electron brought by the hydrogen atom is added to the top of the d bands, and the protonic rigid band model is not quantitatively correct. We also noticed a substantial deformation of the metal d bands upon formation of the hydride, part of the metal d states being found in the structure observed at low energy.

A large increase of the DOS at  $E_F$  is found from the pure intermetallic to its hydride. We obtain  $N(E_F) = 23.93$  states of both spin per Ryd FeTiH; if we ignore the electron-phonon enhancement factor, we find, using the non-interacting electron model, a

**Table 1.** The angular momentum character of the DOS at  $E_F$ ,  $n_l$ , analysed inside the MT spheres. Units are states of both spin per Ryd FeTiH.

	$n_s(l=0)$	$n_p(l=1)$	$n_d(l=2)$
H	0.0430	0.2335	0.0045
Fe	0.2410	0.4545	13.25
Ti	0.1195	0.2870	4.619

theoretical value of the electronic specific heat coefficient  $\gamma = 2.02 \text{ mJ mol}^{-1} \text{ K}^{-2}$ . For pure FeTi, Yamashita and Asano (1972) and Papaconstantopoulos (1975) give respective theoretical values of about  $1 \text{ mJ mol}^{-1} \text{ K}^{-2}$  and  $0.53 \text{ mJ mol}^{-1} \text{ K}^{-2}$ . The increase in the DOS found in the present calculation is in agreement with the trend in the value of  $\gamma$  observed experimentally upon hydrogenation by Hempelmann *et al* (1978) and with the recent magnetic susceptibility data of Stucki (1981) which indicate a substantial increase of the Pauli susceptibility from the pure intermetallic to the hydride. It is to be noted that magnetisation measurements are not trivial to analyse since the magnetisation of superparamagnetic Fe particles gives an important contribution which has to be subtracted.

From the position of the Fermi level which in the hydride falls in rising portion of the DOS we can surmise that the substitution of impurities to the right of Fe in the periodic table could lead to magnetism, in agreement with the observation of Hilscher *et al* (1981).

In table 1 we give a partial wave analysis of the states at the Fermi level, which shows that, although  $E_F$  falls above the valley of the DOS, the Fe d contribution is much larger than the Ti d contribution. This increase in the Fe d character from pure FeTi to FeTiH could explain, together with the effect of lattice expansion, the decrease in the isomer shift of Fe observed experimentally upon hydrogen uptake by Swartzendruber *et al* (1976).

It would be very instructive to compare the theoretical partial wave analysis of the composition of the bands shown in figures 4 and 5 with x-ray L emission bands of both Fe and Ti since, due to the dipole selection rule involved in the oscillator strength matrix elements, useful information on the metal d (and s) character could be obtained by such experiments.

The present theoretical study will hopefully stimulate further experimental investigations which could lead to a full understanding of the electronic properties of these technologically important intermetallic hydrides.

I would like to thank Dr A C Switendick for very useful discussions and Dr L Schlapbach for bringing to my attention and discussing unpublished magnetic susceptibility data.

## References

- Fischer P, Halg W, Schlapbach L, Stucki F and Andresen A F 1978 *Mater. Res. Bull.* **13** 931-46  
 Gupta M 1979 *Solid State Commun.* **29** 47-51  
 Hempelmann R, Ohlendorf O and Wicke E 1978 *Proc. Int. Symp. on Hydrides for Energy Storage, Geilo Norway 1977* (London: Pergamon)  
 Hilscher G, Wiesinger G and Hempelmann R 1981 *J. Phys. F: Met. Phys.* **11** 2167-77

Papaconstantopoulos D A 1975 *Phys. Rev. B* **11** 4801-7

Stucki F 1981 *PhD Thesis* Zürich University

Swartzendruber L J, Bennett L H and Watson R E 1976 *J. Phys. F: Met. Phys.* **6** L331-4

Switendick A C 1978 *Hydrogen in Metals* vol 1, ed G Alefeld and J Völkl (Berlin: Springer) chap 5

Thompson P, Pick P A, Reidinger F, Corliss L M, Hastings J M and Reilly J J 1978 *J. Phys. F: Met. Phys.* **8** L75-80

Yamashita J and Asano S 1972 *Prog. Theor. Phys.* **48** 2119-31