

CHEMICAL BONDING AND ELECTRONIC ANALYSIS OF THE Fe-H INTERACTION

Simonetti S.^{*(1,2)}, Rey Saravia D.⁽¹⁾, Brizuela G.⁽¹⁾, Juan A.⁽¹⁾

⁽¹⁾Departamento de Física, Universidad Nacional del Sur, Av. Alem 1253, 8000 Bahía Blanca, Argentina.

⁽²⁾Centro de Investigaciones en Mecánica Teórica y Aplicada, Universidad Tecnológica Nacional, 11 de Abril 461, 8000 Bahía Blanca, Argentina.

*Fax: 54-291-4595142

E-mail: ssimonet@uns.edu.ar.

Introduction

Scientists and technologists have been studying hydrogen in bulk metals.

Minot and Demangeat have studied the electronic structure of Fe-H on BCC and HCP phases [1]. The results indicate that heat formation is endothermic and the preference location site of H is the tetrahedral site in both geometries.

Jiang and Carter, have reported periodic spin-polarized density functional theory (DFT) predictions of hydrogen adsorption, absorption, dissolution, and diffusion energetics on and in ferromagnetic BCC iron [2].

Teus et al have studied the effect of hydrogen on electronic structure on FCC iron in relation to hydrogen embrittlement of austenitic steels [3].

The interactions of hydrogen with lattice imperfections are important and often determine the H influence on the properties of solids.

Our group has studied the multiple H location in vacancy contained- BCC Fe [4]. The authors suggested that vacancies act as trap sites for hydrogen.

FCC Fe Clusters and Computational Method

In this work, theoretical studies of H in FCC iron structures were addressed. Due to energy interactions, it is performed the comparison of H adsorption in perfect bulk FCC iron with H location in FCC Fe containing a vacancy. The calculations were performed with the YAeHMOP program (Yet Another extended Hückel Molecular Orbital Package) [5].

The perfect and the vacancy contained-FCC structures have been represented by clusters of 180 and 179 metallic atoms respectively (see Fig. 1). We have made the same procedure, majoring the same parameters and comparing the results of H location at the vacancy zone, with H location in the perfect Fe structure.

The most stable position for the hydrogen was found; chemical bond and electronic structure of Fe-H and Fe-Fe interactions were analyzed, before and after H introduction, in the perfect and defective FCC iron structures.

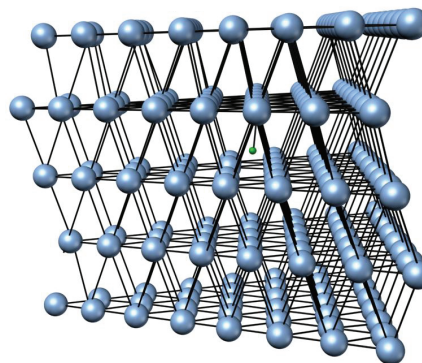


Fig. 1. Schematical view of the Fe_{179+V}-H cluster.

Results and discussion

In the first place we calculate the energy of the system in order to localize the H atom inside the perfect Fe cluster, having the most stable position at -6.52 eV. This was found at 1.741 Å from the Fe first neighbor, and this location in the FCC structure belongs to an octahedral site. Then, we perform calculation for H inside the cluster having a vacancy, majoring a minimum energy of -6.72 eV at 1.617 Å distance from the H closest Fe atom, and to 1.340 Å from the center of the vacancy (see Fig. 1 and 2). Minimum Fe-H distance between 1.4 Å and 1.7 Å were found for multiple H location in vacancy contained- BCC Fe [4].

The interstitial H atom has influence in the Fe first neighbors electronic states density. After the H introduction, the s orbital population from the closest Fe atom has a 9% reduction and simultaneously the population of the p and the d orbitals decrease 8% and 3%, respectively. These are indicating that from the closest Fe atom 4s and 4p orbitals are sharing the main H-Fe interaction. A -0.179 e- charge variation between Fe atoms close to the hydrogen has been observed, while the H atom developed a -0.273 e- charge.

The hydrogen introduction into the Fe-vacancy system also affects the Fe first neighbors, changing their electronic density. The s orbital from the Fe atoms nearest the vacancy decreases the orbital

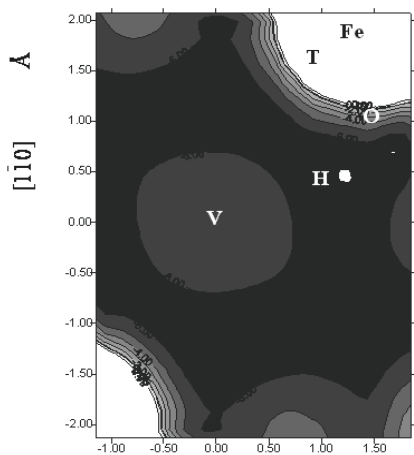


Fig. 2. Energy contour lines for the $\text{Fe}_{179}\text{-V-H}$ system. The vacancy (V), and the octahedral (O) and tetrahedral (T) sites are indicated.

population to about 12% and, the p and d orbital population decreases 2% and 3% respectively, indicating the main participation of the 4s orbitals in the Fe-H bond. A 0.256e- charge variation takes place between the H closest Fe atoms. The H presents a negative charge of -0.328 e- and at the same time a positive charge is given to the Fe first neighbors.

The charge and electronic structure from remote Fe atoms is not affected by the hydrogen presence. We conclude that the H influence is limited to the Fe first neighbors.

COOP curves for the perfect Fe_{180} cluster show the Fe-Fe OP for the Fe closest to H atom decreasing from 0.225 for the cluster without H to 0.158 when hydrogen is present. The OP between Fe atoms decrease about 30%. On the other hand, COOP curves for the $\text{Fe}_{179}\text{-V}$ cluster show the Fe-Fe OP for the Fe closest to hydrogen decreasing from 0.227 for the cluster without H to 0.163 when the H atom is located in the cluster (28%). This reduction is lower than in the perfect Fe cluster.

For the Fe-H interactions in the perfect Fe_{180} cluster, the most of the states are complete, however the antibondings states are pushed up over the Fe 3d band. These states are taking place due H 1s orbital interaction with the Fe 4s and 4p orbitals, with a small contribution of the Fe 3d. The Fe-H overlap population is 0.188.

For Fe-H bond in the $\text{Fe}_{179}\text{-V}$ cluster, again the most of the states are also complete. The bonding states are due to H 1s orbital and Fe 4s orbital, with a small contribution of the Fe 4p and Fe 3d. The -16.5 eV minimum energy value is due mainly to the H1s-Fe4s (see Fig. 3).

Particular, in both cases the COOP curves peaks indicate a strong bonding interaction between H and Fe. Comparing both clusters, based in our calculation, the Fe-H overlap population from the $\text{Fe}_{179}\text{-V}$ cluster is 0.312, larger than in the

perfect Fe_{180} cluster (0.188). The vacancy zone is the most favourable for the Fe-H interaction.

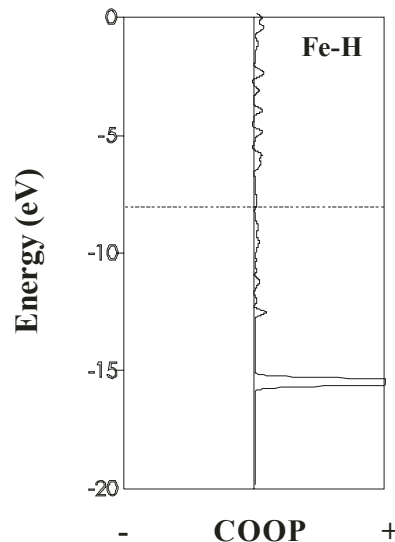


Fig. 3. COOP curve for the Fe-H interaction in the $\text{Fe}_{179}\text{-V-H}$ cluster.

Conclusions

The most stable position for the H atom, in both perfect FCC Fe and FCC Fe containing a vacancy, was determined. We have corroborate through YAeHMOP calculations that in perfect Fe system the octahedral site is energetically favourable, however in the vacancy contained- system the H prefers vacancy region. The Fe-Fe interaction in the metallic matrix for both systems, before and after the hydrogen atom location, was also studied. The changes in the electronic structure was analyzed. We observed a weakness in the Fe-Fe bonds first neighbors to H because the Fe-H interaction is formed. The Fe-H distance was calculated and it is according to the literature.

References

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