

Electronic structure of light impurities in α -Fe and V

Xin-gao Gong^{†‡}, Zhi Zeng[§] and Qing-qi Zheng[§]

[†] International Centre for Theoretical Physics, Trieste, Italy

[§] Institute of Solid State Physics, Academia Sinica, People's Republic of China

Received 17 August 1987, in final form 3 April 1989

Abstract. The electronic structure of α -Fe and V with H and C as impurities is calculated using the embedded-cluster model in the framework of self-consistent local-density theory. The results obtained reveal that charge transfer between the H atom and the host atoms is small, but the magnetic moments of neighbouring Fe atoms are reduced. The results of the total energy calculation show that H in α -Fe prefers to occupy the octahedral interstitial site. On the contrary, there is some charge transfer between the C atom and the host atoms. The distance between the C and nearest-neighbour Fe atoms is elongated 23%. The interaction between the H and the C impurities was studied using a set of clusters of Fe_{10}CH in which the atoms were located in five kinds of configuration. The energy of clusters with H on the octahedral interstitial site is lower than that on the tetrahedral interstitial site.

1. Introduction

The study of H in Fe is a topic of continuing interest, especially with respect to the problem of H embrittlement in Fe and steel. Because of the very low solubility of H in Fe, it is difficult to investigate experimentally with sufficient accuracy and, until now, some fundamental problems are still the subject of argument. The hyperfine field at the tetrahedral interstitial site (T site) in pure α -Fe calculated from the neutron scattering form factor is negative (-0.11 T), while that at the octahedral interstitial site (O site) is positive [1]. A negative hyperfine field (-1.06) has been reported in [2, 3] from the spin-relaxation experiments. Therefore, it was suggested in [2] that the muon, which may be thought of as a light isotope of H, occupies the T site in α -Fe. However, the existence of the muon (or H atom) will cause a local charge redistribution around it and hence will change the hyperfine field at this position. This effect was not sufficiently considered in the interpretation in [2]. In fact, it was reported in [4] that the calculated hyperfine fields experienced by the muon in α -Fe are -1.40 T and -1.08 T for the T site and the O site, respectively. In order to clarify these problems further, in this work the electronic structure and total energy of H atoms in α -Fe are studied using the embedded-cluster models of Fe_{10} (bulk like), Fe_{10}H (O site) and Fe_{10}H (T site) (figure 1(a)).

C atoms which are a common impurity in Fe play an important role in the physical properties of Fe. The electronic structure of C in α -Fe has been studied in [5], using an unrelaxed cluster with C in the substitutional position, in the framework of the X_α scatter wave method. It is well known that C atoms in α -Fe are in the octahedral position and cause a large local distortion, which was neglected in [5]. In this work, clusters with

[‡] Permanent address: Institute of Solid State Physics, Academia Sinica, People's Republic of China.

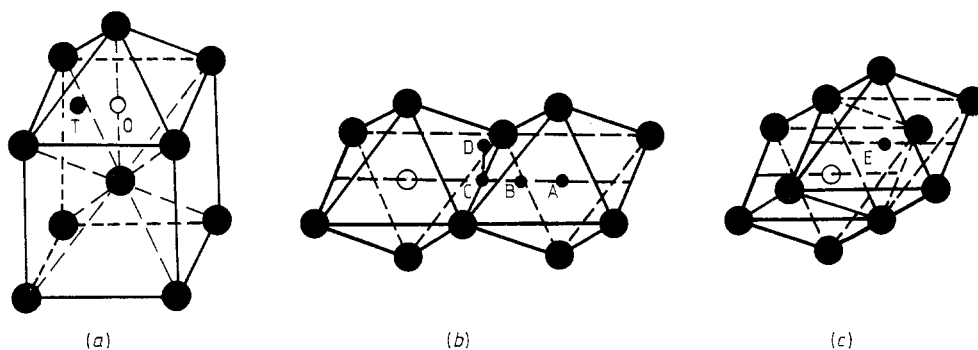


Figure 1. (a) $M_{10}L$ cluster ($M = \text{Fe or V}$; $L = \text{C or H}$). T and O in the cluster indicate the T site and O site, respectively. (b) Fe_{10}CH clusters (positions B and D for T-site H, and positions A and C for O-site H). (c) Fe_{10}CH cluster (position E for O-site H).

different distances between the C atom and its nearest-neighbour Fe atoms were used to calculate the electronic structure and total energy.

The H in the metal may favour sites near the interstitial or substitutional impurities; this is the so-called trapping effect. The study of the trapping of H in Fe is of practical interest to industry. In order to reach a better understanding of the H-trapping mechanism in $\alpha\text{-Fe}$, the interaction between H and C impurities with different relative locations of atoms in $\alpha\text{-Fe}$ was considered.

2. Models and theoretical method

A self-consistent calculation was performed using the local-density approximation which has been discussed in detail elsewhere [6]. In this work the spin-polarised exchange-correlation potential $V_{xc}(\rho_\sigma)$ can be written as follows:

$$V_{xc}(\rho_\sigma) = -3\alpha(\frac{2}{3}\rho_\sigma)^{1/3}.$$

The electron density is a sum over the spin orbitals of clusters with occupation number $N_{j\sigma}$

$$\rho_\sigma(r) = \sum_j N_{j\sigma} \psi_{j\sigma}^* \psi_{j\sigma}.$$

The cluster orbitals are expanded in a set of symmetry orbitals which are composed of numerical atomic functions. The frozen-core electron procedure was used and the valence electron orbitals for the basis set included the 3d and 4s orbitals of Fe and the 1s orbital of H. In this work, we used the wavefunction of atoms in a certain kind of potential well to simulate the environment of the crystal. The agreement between the calculated densities of states (DOSS) for the Fe_{10} (pure Fe) cluster calculation and the band theory calculation is good, as shown in figure 2,

An embedded-cluster method was used to take into account the influence of atoms outside the cluster. In all the calculations, the embedded potential is generated by atoms in a 125-unit cell around the cluster. In this work the finite clusters of Fe_{10} , Fe_{10}H , V_{10}H and Fe_{10}CH were used. Two different sites for H in the cluster were calculated; one is the T site and the other is the O site. C atoms in $\alpha\text{-Fe}$ are located at O sites, and the C

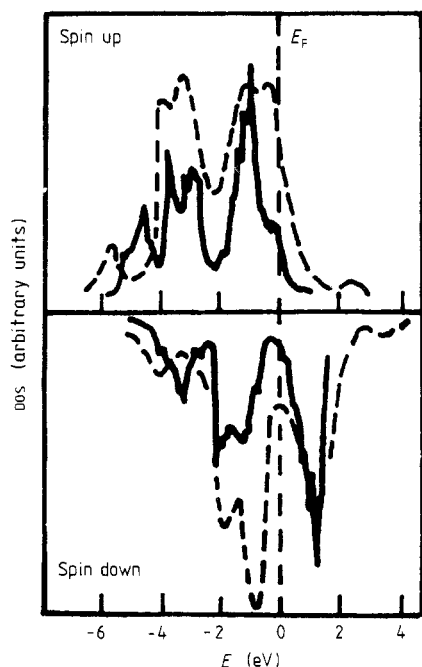


Figure 2. The total DOS obtained by the cluster method in this work for a pure Fe cluster (---) and by the band theory method (—).

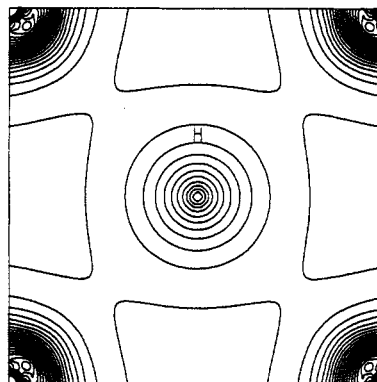


Figure 3. The contour map of the charge density of an Fe_{10}H (O-site) cluster in the (100) plane.

would produce relaxation of its neighbouring Fe atoms. In this work, we investigated the effects of the relaxation of Fe atoms using various clusters with different distances between the C atom and its nearest-neighbour atoms. The equilibrium atomic structure was found at total energy minimum. All the clusters are shown in figure 1.

3. Results and discussion

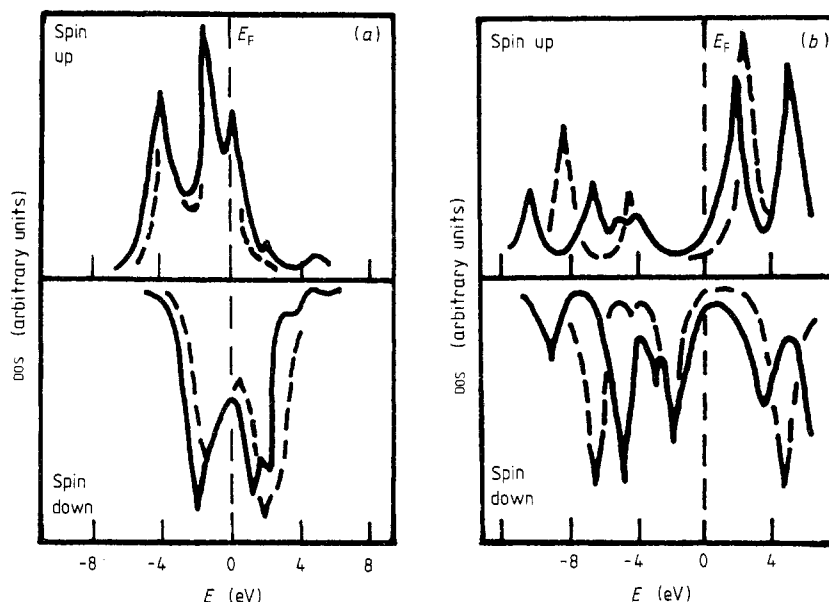
3.1. Properties of H impurities in α -Fe and V

In order to check our cluster model, the DOS of the Fe_{10} cluster for Fe crystals is compared with the results of the band theory calculation in figure 2. From figure 2, one can see that the agreement between our results and that obtained by the band theory calculation [7] is good. In [5] it was reported that a larger cluster led to a resultant DOS closer to the band theory results. Our calculation reveals that the embedded-cluster procedure can reduce the size effect of the cluster model. The obtained magnetic moments of the centre atom are $2.23\mu_B$ and $-0.10\mu_B$ respectively, which is in agreement with experimental values.

Calculations on the V_{10}H clusters, with H at the O site and at the T site were made using the spin-restricted DV- X_α method. There are 0.28 electron and 0.34 electron transferred from the host atoms to the H atom for the O-site and the T-site cases, respectively. The total energy of the V_{10}H (O-site) cluster is 2 eV higher than that of the V_{10}H (T-site) cluster. This result is in agreement with the conclusions in [8] that the H atom in V is located at the T site, although the energy difference of 2 eV from our calculations is a little too large.

Table 1. The calculated magnetic moments of Fe and H atoms.

Cluster	Magnetic moment		
	H 1s	Fe 3d	Fe 4s
Fe ₁₀ (pure Fe)	—	2.23	−0.12
Fe ₁₀ H (T site)	−0.15	1.64	−0.12
Fe ₁₀ H (O site)	−0.12	1.32	−0.12

**Figure 4.** (a) The 3d partial DOS of the Fe atom, in an Fe₁₀ (pure Fe) cluster (---) and in an Fe₁₀H (O-site) cluster (—). (b) The 4s partial DOS of the Fe atom, in an Fe₁₀ (pure Fe) cluster (---) and in an Fe₁₀H (O-site) cluster (—).

For the Fe₁₀H (O-site) and Fe₁₀H (T-site) cluster, there are 1.12 electrons and 1.16 electrons for the T-site and O-site H atom, respectively, so that neither the proton model nor the anion model for H atoms, in α -Fe is suitable. A typical charge-density contour map in the (100) plane containing the O-site H atom is shown in figure 3. From the figure we can see that the T-site or O-site proton attracts the s-like electron with a negative spin at this interstitial site and causes a dramatic enhancement of the negative hyperfine field. This is why the hyperfine field experienced by the muon at the T site and O site is negative.

The presence of H reduces the magnetic moments of neighbouring Fe atoms. A comparison of the magnetic moments of Fe and H atoms for Fe₁₀, Fe₁₀H (T-site) and Fe₁₀H (O-site) clusters in pure Fe are listed in table 1. Typical partial DOSs of the 3d and 4s electrons of Fe atoms in the Fe₁₀ and Fe₁₀H (O-site) clusters are shown in figure 4. One can see from figure 4 that the presence of H in Fe lowers the 3d levels with a negative spin; therefore the number of negative-spin 3d electrons increases and the magnetic moments of neighbouring Fe atoms decrease. There is an explicit change in the partial DOS of 4s electrons of Fe atoms. This implies that the electrons of H atoms interact mainly

Table 2. The Mulliken populations of C atoms in Fe_{10}C clusters.

a/a_0 (%)	Q_{elec}	
	2s	2p
0	1.51	3.41
20	1.63	3.20
30	1.69	3.11

with the 4s electrons of Fe atoms, and the interaction between the 3d electrons of Fe and the 1s electron of H is indirect. The total energy of the Fe_{10}H (O-site) cluster is 0.11 eV lower than the energy of the Fe_{10}H (T-site) cluster; hence, from the viewpoint of energy, H atoms in α -Fe can more easily occupy the O site rather than the T site. If we assume that H atoms occupy the O site in α -Fe, the relatively large muon diffusion coefficient can also be interpreted.

3.2. Properties of C atoms in α -Fe

In this work the relaxation of the lattice induced by C atoms at the O site is considered where clusters increase the distance between the C and nearest-neighbour Fe atoms by 0%, 20% and 30% along the fourfold symmetry axis. For these three cases, the Mulliken populations of C atoms are presented in table 2. From this table, one can see that about 0.85 electron is transferred to the C atom. The atomic character of the 2s electrons of the C atoms remains nearly unchanged; on the contrary there is a strong interaction between the 2p electrons of the C atoms and the 3d and 4s electrons of the neighbouring Fe atoms. The 2p electrons of the C atoms have mixed with the 3d and 4s orbitals of the neighbouring Fe atoms. This mixing increases with increasing distance between the C and Fe atoms. This indicates that the cause of local relaxation induced by C impurities is partially related to the bond between the C and Fe atoms. The important effects of relaxation on the partial DOS for the 3d levels are shown in figure 5. Because of the presence of C atoms the magnetic moments of nearest-neighbour Fe atoms (the centre atom) are reduced, from $2.23\mu_B$ for the bulk-like cluster to $1.10\mu_B$, $1.46\mu_B$ and $1.22\mu_B$ for the unrelaxed, the 20% relaxed and the 30% relaxed clusters, respectively.

A total energy minimum of the cluster is obtained with 23% increase in distance between C and the two nearest-neighbour Fe atoms, which corresponds to stable relaxation. This result is in agreement with the experimental measurements [9]. In this calculation, we did not take into account the relaxation of the second-nearest neighbours, but from experimental results the relaxation of second-nearest neighbours is only 10% of the relaxation of nearest neighbours. So we expect that the effects from relaxation of second-nearest neighbours are not large.

3.3. Interaction between H and C atoms in α -Fe

The interaction between C and H in Fe is considered using the embedded clusters of Fe_{10}CH with five kinds of relative location of C, H and Fe atoms as shown in figure 1. The results indicate that there is less direct interaction between C and H atoms in all five cases. In figure 6 a typical contour map of charge density for the E and A position clusters show that there is no direct binding between H and C atoms. The total energy of these

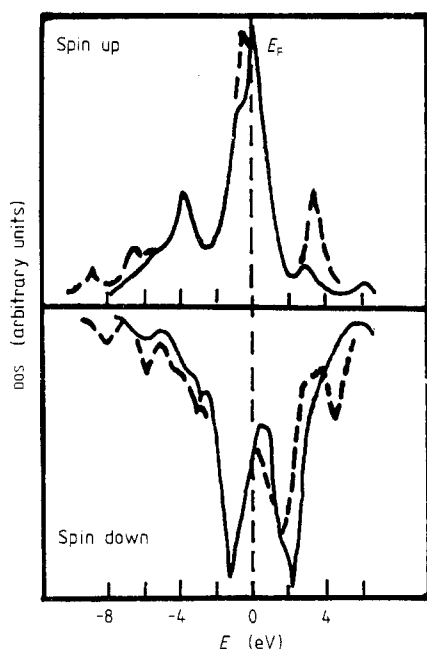


Figure 5. The 3d partial DOS of Fe in unrelaxed and relaxed Fe_{10}C cluster.

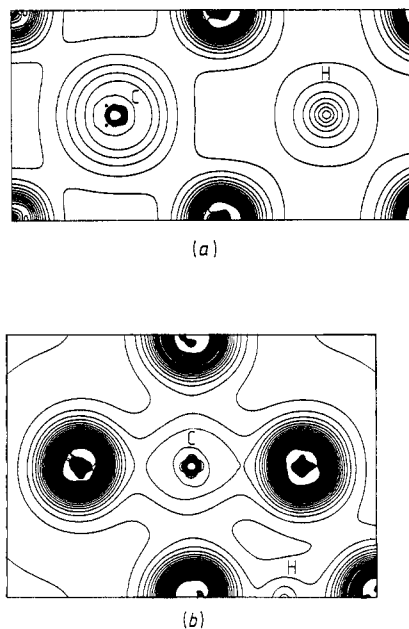


Figure 6. Charge density of a Fe_{10}CH cluster: (a) H in position A; (b) H in position E.

five clusters shows that the clusters with O-site H (positions A, C and E in figure 1) have lower energy. This supports the conclusion about the possibility that H atoms occupy the O site rather than the T site in $\alpha\text{-Fe}$. In the largest-binding-energy cluster at position E, the positions of H and C are on one body cubic diagonal. Similar results were obtained in [10], although T-site H (which in our opinion may be unsuitable) was used. Calculations were also made on relaxed clusters which have a lower energy, but these did not change the conclusion obtained with unrelaxed clusters.

References

- [1] Shull C G and Mook H H 1966 *Phys. Rev. Lett.* **16** 184
- [2] Seeger A 1976 *Phys. Rev. A* **58** 137
- [3] Nishida N, Hadyano R S, Nagamina K, Yanazaki T, Brewer J H, Garnar D M, Fleming D G, Takauchi T and Tshikawa Y 1977 *Solid State Commun.* **22** 235
- [4] Lindgren B and Ellis D E 1982 *Phys. Rev. B* **26** 636
- [5] Lee K, Callaway J, Kwong K, Tang R and Ziegler A 1985 *Phys. Rev. B* **31** 1796
- [6] Cao P L, Ellis D E, Freeman A J, Zheng Q Q and Bader S D 1984 *Phys. Rev. B* **30** 4146
- [7] Moruzzi V L, Janak J F and Williams A R 1978 *Calculated Electronic Properties of Metals* (Oxford: Pergamon)
- [8] Darby M I and Reed M N 1983 *J. Less-Common Met.* **91** 109
- [9] Swartz J C, Swilling J W and Schwoeble A J 1968 *Acta Metall.* **16** 1359
- [10] Shirley A I and Halk C K 1983 *Scr. Metall.* **17** 1003