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## Magnetic moments and hyperfine fields in hydrogenated Fe–V alloys

M E El Zain† and B Lindgren‡

† Physics Department, Faculty of Science, Sultan Qaboos University, PO Box 32486, Al-Khod, Sultanate of Oman

‡ Department of Physics, Box 530, S-751 21 Uppsala, Sweden

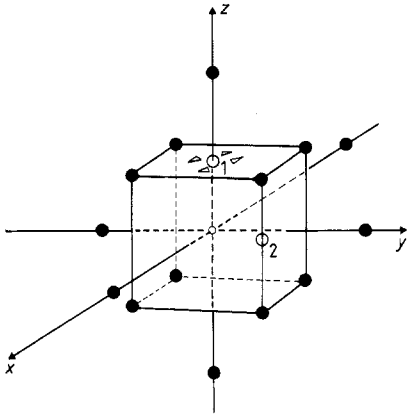
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**Abstract.** The first principle discrete variational method is employed to calculate the local magnetic moment  $\mu_{\text{Fe}}$ , the valence contact spin density  $\Delta\rho_v(0)$ , magnetic hyperfine field  $B$  and valence charge  $\rho_v(0)$  at central Fe sites in  $\text{FeV}_{1-x}\text{H}_x$  clusters representing hydrogenated dilute Fe–V alloys. These quantities were found to depend on the type of the interstitial site occupied by hydrogen where tetrahedral and two kinds of octahedral sites were considered. The occupation of octahedral sites ( $\text{O}_1$ ) closer to the Fe central atom was found to reduce  $\mu_{\text{Fe}}$ ,  $\Delta\rho_v(0)$ ,  $B$  and may or not reduce  $\rho_v(0)$  whereas the octahedral sites closer to V atoms ( $\text{O}_2$ ) led to increase in  $\mu_{\text{Fe}}$ , decrease in  $\rho_v(0)$  and left  $\Delta\rho_v(0)$  and  $B$  almost unchanged. A correlation is made of the relevance of these calculations to experimental results on hydrogenated Fe–V alloys.

### 1. Introduction

It is observed that addition of non-magnetic impurities to ferromagnetic transition metals leads to reduction of average magnetic moment  $\mu$ , and contact hyperfine field  $B$ . In many cases both quantities were found to vanish at some critical concentration. However, in principle,  $\mu$  and  $B$  measure different properties of magnetic materials. While a finite average magnetic moment is an indication of existence of long range ferromagnetic order, the hyperfine field gives the local spin density at probe site (when the Fermi contact term dominates). However, it is widely believed that a non-zero  $\mu$  implies a non-zero  $B$  and vice versa.

Fe–V alloys were not an exception. Both  $\mu$  and  $B$  were found to vanish at about 70% at V concentration (Nevitt and Aldred 1963, Shiga and Nakamura 1978). Three models were put forward as candidates to explain magnetism in Fe–V alloys. In essence, the first model assumes a regular decrease, to zero, of Fe moment as V concentration increases. This model received theoretical support from the work of Johnson *et al* (Johnson *et al* 1987) where the KKR-CPA method was employed. In the second model (Jaccarino-Walker model (Jaccarino and Walker 1965)), the Fe moment vanishes when an Fe atom is surrounded by four or more V atoms at any V concentration, and HF-CPA calculations conform with this line (Hamada and Miwa 1978). The third model, where a randomly oriented, but finite Fe moment is retained at any V concentration, was rejected by Shiga and Nakamura on the basis of absence of magnetic splitting in  $^{57}\text{Fe}$  Mössbauer spectra. However, a modified version of this model has been proposed by



**Figure 1.** The 15-atom cluster with octahedral and tetrahedral hydrogen sites ( $\circ$ ) represent the central Fe atom and ( $\bullet$ ) the V atoms in the first and second shells ( $\circ_1, \circ_2$ ) are symmetrical positions representing H octahedral sites ( $\triangle$ ) are symmetrical positions representing H tetrahedral sites.

El Zain and Ellis (El Zain and Ellis 1987), since it has been shown that (El Zain *et al* 1986) B at  $^{57}\text{Fe}$  sites can be zero in spite of a retained large Fe moment.

Through specific heat and magnetic susceptibility measurements, it was observed that addition of H to Fe–V alloys, in paramagnetic phase, results in a transition to ferromagnetic phase at about 5.6 electrons per atom (Obermann *et al* 1976, Ohlendrof *et al* 1979), exactly as the addition of Fe would produce. Such a transition was not observed in  $^{57}\text{Fe}$  Mössbauer measurement (Ostrasz *et al* 1986, Ostrasz and Suszkiewicz 1987). Instead, the observed small broadening in the Mössbauer spectra was attributed to quadrupole splitting resulting from departure of perfect BCC structure as H is added.

The problem then amounts to envisaging a situation where addition of a non-magnetic element to a non-magnetic material induces a magnetism that is detectable by some means and not by intimate others. The objective of this work is to look for possible explanation of this enigma. In the following section we present the computational model we used. Then the results are presented and discussed in §3. Concluding remarks are given in §4.

## 2. Computational model

The first principle discrete variational method, which is well documented in the literature (Averill *et al* 1973, Baerends *et al* 1973, Rosen and Ellis 1976), is used to calculate the electronic and magnetic properties of Fe–V–H clusters shown in figure 1. The Fe and V reside on the regular BCC lattice points while H enters as an interstitial at octahedral ( $\circ$ ) and tetrahedral ( $\tau$ ) sites. We considered  $\circ$  and  $\tau$  sites close to the central atom only. There are two types of  $\circ$  sites: those at symmetrical points  $(0, 0, a/2)$  (denoted by  $\circ_1$ ) and those at the symmetrical points  $(a/2, a/2, 0)$  (denoted by  $\circ_2$ );  $a$  being the lattice constant.  $\circ_1$  and  $\circ_2$  sites are at a distance of  $a/2$  and  $a/\sqrt{2}$  from the central atom respectively. The tetrahedral sites are at  $a(0, a/4, a/2)$  and the corresponding symmetrical positions on the faces of the cube.

The spin polarised local density approximation with a von Barth-Hedin exchange-correlation potential was used. The self-consistent computation was performed using as variational basis a linear combination of atomic orbitals (LCAO) of 3d, 4s and 4p for transition metal atom and 1s for hydrogen atom. Double basis, where atomic orbitals resulting from  $3d^4 4s^1$  and  $3d^4 4s^0 4p^0$  configurations, were employed for the Fe atom when

**Table 1.** The total magnetic moment  $\mu_{\text{Fe}}$  in Bohr magnetons, the valence spin density  $\Delta\rho_v(0)$  in au, the valence contribution hyperfine field  $B_v$  in T, the contact magnetic hyperfine field  $B$  in T and charge density  $\rho_v(0)$  in au at the central Fe atom for Fe<sub>15</sub>, Fe-V and Fe-V-H clusters. Hydrogen enters at interstitial sites O<sub>1</sub>, O<sub>2</sub> and T as explained in the text.

	Fe <sub>15</sub>	FeV <sub>14</sub>	FeV <sub>14</sub> H <sub>2</sub> (O <sub>1</sub> )	FeV <sub>14</sub> H <sub>4</sub> (O <sub>1</sub> )	FeV <sub>14</sub> H <sub>4</sub> (O <sub>2</sub> )	FeV <sub>14</sub> H <sub>8</sub> (O <sub>2</sub> )	FeV <sub>14</sub> H <sub>8</sub> (T <sub>2</sub> )
$\mu_{\text{Fe}}$ ( $\mu_B$ )	2.12	2.33	0.84	1.08	2.45	2.50	1.64
$\Delta\rho_v(0)$ (au)	-0.13	+0.24	+0.18	+0.15	+0.24	+0.24	+0.20
$B_v$ (T)	-6.8	+12.6	+9.4	+7.9	+12.6	+12.6	+10.5
$B$ (T)	-29.8	-9.8	-1.6	-3.1	-11.1	-11.8	-4.5
$\rho_v(0)$ (au)	5.61	6.30	5.62	6.27	5.70	5.16	4.91

it was in the center of a cluster. This was found to give better hyperfine fields. Potential wells of radius 5 au and depth of  $-0.2$  au were used for V and other Fe atoms while no well was used for H atoms.

The local electronic charge density is given by

$$\rho_{\sigma}(\mathbf{r}) = \sum_k n_{k\sigma} |\psi_{k\sigma}(\mathbf{r})|^2 \quad (1)$$

where  $n_{k\sigma}$  is the occupation number of the molecular orbital  $\psi_{k\sigma}(\mathbf{r})$  for spin  $\sigma$  and the  $k$ th energy level. The total cluster charge density at position  $r$  is  $\rho_{\sigma}(\mathbf{r}) + \rho_{-\sigma}(\mathbf{r})$ .

To calculate the potential the total charge density was cast in a multicenter-overlapping multipolar form (Delly and Ellis 1982):

$$\rho_{\text{model}}(\mathbf{r}) = \sum_{nlm} d_{jlm}(n) \rho_j(|\mathbf{r} - \mathbf{r}_n|) Y_{lm}(r_n) \quad (2)$$

The radial density basis set  $\{\rho_j\}$  was constructed from spherical atomic densities, calculated from the wavefunction variational basis and from seven parabolic radial functions for each  $l = 0$  in the fully symmetric representation of the molecular point group. The coefficients  $\{d\}$  were determined by least square fitting to the total cluster charge density. The magnetic hyperfine field at the Fe site was calculated from the phenomenological relation

$$B = -A\mu_d + C(\rho_{\uparrow}(0) - \rho_{\downarrow}(0)) \quad (3)$$

where the first term represents the core contribution and the second the valence part.  $\mu_d$  is the local 3d moment and a value of  $10 \text{ T}/\mu_B$  was taken for the constant  $A$  (Blugel *et al* 1987, El Zain *et al* 1986).  $\rho_{\sigma}(0)$  is the valence part of the spin density and  $C = 52.4$  when  $B$  is in tesla and  $\rho$  in au.

### 3. Results and discussion

We have calculated the total magnetic moment (using Mulliken population analysis), the charge and spin densities and the magnetic hyperfine field (using 3 above) at the central Fe atom. The results are given in table 1. The Fe<sub>15</sub> cluster represent Fe atoms in  $\alpha$ -Fe. The FeV<sub>14</sub> cluster represent a Fe atom in V at very low Fe concentration. The

clusters  $\text{FeV}_{14}\text{H}_n$  ( $\text{O}_1$  or  $\tau$ ) represent different numbers ( $n$ ) of hydrogen atoms at different location.

The magnetic moment at the Fe site in the Fe15 cluster agrees quite well with band calculations (Callaway and Wang 1977) and experimental results (Danan *et al* 1968) while the magnetic hyperfine field is slightly less in magnitude. This is to be expected since  $B$  is more sensitive to the nature of the atomic basis and the accuracy in the numerical integration. However, the valence contribution to  $B$  is similar to that found by band methods. Furthermore, the valence contact charge density agrees with experimental (Shinohara and Fujioka 1973) and band (Callaway and Wang 1977) results.

The  $\text{Fe}_{15}$  cluster results and their close comparison to experimental and other theoretical calculations give confidence on the results of Fe–V and Fe–V–H clusters as representative of the corresponding bulk materials. However, for the last clusters there are still two parameters which are still fairly arbitrary. These are the lattice constants and the atomic site occupations.

In choosing the lattice constants we were guided by a recent X-ray diffraction result (Ostrasz *et al* 1986) which showed that the Fe–V lattice is distorted from BCC to BCT on addition of H; and the lattice parameters changed from  $a = 3.01 \text{ \AA}$  at 0 at. % H to  $a = 2.95 \text{ \AA}$ ,  $c/a = 1.14$  at 5.8 at. % H.

The experimental measurements were performed on alloys of low Fe content ( $\approx 4$  at. % at Fe). Hence, if Fe distribution in V is homogeneous the most dominant configuration would be that in which Fe is surrounded by V in at least the first and second shells of neighbours. This legitimatises the use of  $\text{FeV}_{14}$  cluster as a representative of these Fe–V alloys.

The  $\text{FeV}_{14}$  cluster results confirm our previous finding (El Zain *et al* 1986). The magnetic moment at Fe sites is large and even larger than that of a  $\text{Fe}_{15}$  cluster, while  $B$  is smaller in magnitude (but not zero in this case). The contact charge density is greater than in a  $\text{Fe}_{15}$  cluster implying a negative isomer shift of order  $-0.2 \text{ mm s}^{-1}$  which is comparable to experimental results (Dübiel and Zinn 1983). We take the results of this cluster as a reference to compare the trends in Fe–V–H clusters with.

A quick reflection on the table then shows that H at  $\text{O}_1$  and  $\text{O}_2$  sites influences the properties of the central Fe atom differently, whereas H at  $\tau$  site has an intermediate effect.

The first result for  $\text{O}_1$  sites is due to 2 hydrogen atoms placed along the  $z$ -axis on the horizontal faces of the cube of nearest neighbours. The second is due to 4 hydrogen atoms on the vertical faces. We note that for  $\text{O}_1$  occupation the total magnetic moment at the central Fe site is less than the hydrogen free case. The spin density at the nuclear site is also reduced. The contact hyperfine field is almost zero. The contact charge density is decreased in the first case and increased in the other.

The first and second results when  $\text{O}_2$  sites are occupied are due to 4 hydrogen atoms on the vertical edges and 8 atoms on the horizontal edges respectively. In both cases the total magnetic moment at the central Fe atom is relatively large compared to that of  $\text{FeV}_{14}$  cluster, while the contact spin density is of comparable value.  $B$  is slightly larger in magnitude. The contact charge density decreases with increasing number of H atoms.

When the  $\tau$  site is occupied the results are intermediate between those corresponding to  $\text{O}_1$  and  $\text{O}_2$  occupation. However, the decrease in contact charge density is comparable to that of  $\text{O}_2$  occupation.

In the following we will look first for reasons behind the different characteristics obtained when H occupies different interstitial sites and then secondly at the relevance of these results to experimental interpretation.

The hydrogen 1s orbital belongs to the most symmetric alg.1 representation of the d4h point group employed for Fe-V and Fe-V-H clusters. It mixes with the 4s and 3d<sup>(0)</sup> orbitals of the central Fe atom (and of course with some other orbitals from outer atoms). It was found that the overlap between the 1s H orbital and 3d<sup>(0)</sup> of the central Fe atom is about an order of magnitude larger for O<sub>1</sub> occupation as compared to O<sub>2</sub>.

The energy level occupation is such that the 6th state of alg.1 representation is occupied for spin up and empty for spin down in the case of FeV<sub>14</sub> clusters. Addition of H in general lowers the energy levels of states belonging to alg.1 representation. When 2 H atoms were added at O<sub>1</sub> both 6th states were then occupied and hence the net spin density is decreased. Similarly was the case of 4 H atoms at O<sub>1</sub>. But in this case a large 4s Fe-1s H overlap was obtained leading to a larger contact charge density. However, for H at O<sub>2</sub> the 6th spin down state remained empty while the 7th spin up started to be occupied resulting in spin increase.

The relevance of these calculations to understanding experimental results of hydrogenated Fe-V alloys rests upon the model presented by El Zain and Ellis (El Zain and Ellis 1987). In that model the Fe moment is constant and positive while the V moment varies from negative to positive values depending on the local environment. At low Fe concentrations, the average moment was vanishingly small. Then if H can tip the balance in favour of one direction a net non-zero average magnetic moment will be produced. This is in fact what happens when hydrogen occupies the O<sub>2</sub> sites. In this case it is not only that the Fe moment increases but also the oppositely oriented V moment at nearest neighbour shell decreases in magnitude. To this end, we performed calculation on two clusters in which V was taken as the central atom with 8 Fe atoms at the NN shell and 6 V atoms at the NNN shell. H occupied O<sub>1</sub> and O<sub>2</sub> sites relative to Fe atoms in the first shell for the two respective clusters. The magnetic moments at the central V sites were  $-1.8 \mu_B$  and  $-1.3 \mu_B$  for O<sub>1</sub> and O<sub>2</sub> occupation respectively. This was so although the Fe moment in the first shell is about 30% greater for O<sub>2</sub> cases as compared to O<sub>1</sub>. Since the V moment is induced by Fe one would have expected the V moments to be in opposite order had it not been for the presence of H.

The presence of H at O<sub>2</sub> sites would also serve as a bridge connecting the Fe moment with the parallel oriented V moment on the next nearest neighbour shell. H at the O<sub>2</sub> site in fact acquired a minute positive moment ( $\approx 0.03 \mu_B$ ) while a zero moment was found when H occupied O<sub>1</sub> or T sites.

Thus on addition of H to Fe-V alloys, we suggest that, the O<sub>2</sub> sites become occupied leading to a net average magnetic moment which can be detected by specific heat and magnetic susceptibility measurements. The Mössbauer spectra would still be comparable to that of hydrogen free Fe-V alloys. Hence, no or only very small magnetic splitting will be detected.

#### 4. Conclusion

The local magnetic moment, contact spin density, hyperfine field and charge density have been calculated for hydrogen free and hydrogenated Fe-V systems.

It was found that these quantities vary greatly as different interstitial sites are occupied by hydrogen. This is explained in terms of varying strength of overlap between the 1s hydrogen orbital and the 3d<sup>(0)</sup> orbital of the central Fe atom.

Furthermore, the occupation of a particular octahedral site,  $O_2$ , by hydrogen led to trends that would explain the observed experimental properties. In this case a ferromagnetic phase is expected to be created by addition of hydrogen to paramagnetic Fe-V alloys. The presence of this ferromagnetic phase can be detected through specific heat and magnetic susceptibility measurements but not through Mössbauer spectroscopy.

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